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THE  
LONDON, EDINBURGH, AND DUBLIN  
PHILOSOPHICAL MAGAZINE  
AND  
JOURNAL OF SCIENCE.

CONDUCTED BY

SIR ROBERT KANE, LL.D. F.R.S. M.R.I.A. F.C.S.

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AND

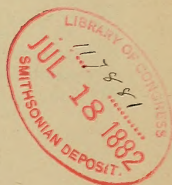
WILLIAM FRANCIS, PH.D. F.L.S. F.R.A.S. F.C.S.

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"Nec araneorum sane textus ideo melior quia ex se fila gignunt, nec noster vilior quia ex alienis libamus ut apes." JUST. LIPS. *Polit. lib. i. cap. 1. Not.*

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VOL. XIII.—FIFTH SERIES,  
JANUARY—JUNE 1882.



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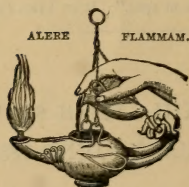
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"Meditationis est perscrutari occulta; contemplationis est admirari perspicua . . . . Admiratio generat quæstionem, quæstio investigationem, investigatio inventionem."—*Hugo de S. Victore.*

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—"Cur spirent venti, cur terra dehiscat,  
Cur mare turgescat, pelago cur tantus amaror,  
Cur caput obscura Phœbus ferrugine condat,  
Quid toties diros cogat flagrare cometas,  
Quid pariat nubes, veniant cur fulmina cœlo,  
Quo micet igne Iris, superos quis conciat orbes  
Tam vario motu."

*J. B. Pinelli ad Mazonium.*





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## ERRATUM IN VOL. XI.

Page 414, *for* E. H. Nichols *read* E. L. Nichols.

## ERRATA IN VOL. XII.

Page 370, second line from bottom, *for* maximum velocity *read* maximum rate of change of velocity  
— 371, second line from top, *for* kinetic energy *read* acceleration

## ERRATA IN VOL. XIII.

- Page 45, end of art. 45, *for*  $+e_2$  *read*  $-e_2$   
— 46, art. 50, line 6, end of numerator *for*  $\frac{3}{2^n}$  *read*  $\frac{3}{2^n} J$   
— 46, art. 52, line 4, *for* (13) *read*  $f(D)_z + x^3 F(D)_z = 0$  . (14)  
— 46, art. 52, line 5, *for* (13) *read* (14).  
— 135, last line of text, in equation (7), *for*  $\frac{\Theta}{\Theta_c}$  *read*  $\frac{\Theta_c}{\Theta}$
- 

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- X. Illustrative of Mr. L. Fletcher's Crystallographic Notes.

THE

LONDON, EDINBURGH, AND DUBLIN

# PHILOSOPHICAL MAGAZINE

AND

## JOURNAL OF SCIENCE.

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[FIFTH SERIES.]

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JANUARY 1882.

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I. *On the Electrical Resistance of Vacuum.* By E. EDLUND,  
*Professor of Physics at the Swedish Royal Academy of  
Sciences\*.*

### § 1.

IT has been generally assumed that a vacuum presents a total absence of electric conductivity; and there are experiments dating from long ago which seem to favour the truth of this opinion. A multitude of researches have been made from time to time, with the view of discovering the real state of the question. This last is, indeed, of the greatest importance in several respects. The heavenly bodies are separated from one another by space in which, as far as we know, no other matter exists but the luminiferous æther. It is a fact generally known at the present time that the solar spots exert a sensible influence upon the aurora borealis and the magnetic condition of the earth, or that all these phenomena derive their origin from a common cosmic cause. Now, if the space between the celestial bodies were perfectly non-conducting, it would be difficult to conceive the possibility of a direct correlation between those phenomena; indeed it would hardly be possible that an appreciable action of electrical induction should assert itself at so great a distance. And it is quite as impossible to see, in the correlation observed, a secondary action of the insignificant modification of the thermal

\* Translated from a copy, communicated by the Author, of a memoir presented to the Swedish Royal Academy of Sciences on the 23rd of April 1881, *Kongliga Svenska Vetenskaps-Akademiens Handlingar*, Bandet xix. no. 2.

radiation which could be produced by the variable number and size of the sun-spots. It is henceforth difficult to doubt that the auroræ boreales owe their production to electric currents passing through the terrestrial atmosphere; but there has sometimes been observed an auroral light originating at a height so considerable above the earth's surface that the tenuity of the air at that altitude must far exceed that which it is possible to produce by means of the best apparatus of our laboratories. This auroral light shows that the rarefied air of those high regions must necessarily be conductive, seeing that it transmits electric currents, although the experiments of our laboratories lead to the admission that air of corresponding density is a nonconductor of electricity\*. The question whether electricity needs or does not need any ordinary ponderable matter in order to propagate itself from one place to another has been much discussed, and is of great importance when viewed from the standpoint of theory. If a satisfactory answer could be made to it, the question of the electrical resistance of vacuum would also, of course, be found solved. It is, unfortunately, impossible to produce an absolute vacuum, so as to solve the said question by a simple experiment;

\* Warren De La Rue and H.W. Müller could not, with a battery of 11,000 elements, make the current pass through hydrogen of which the pressure was 0.000055 millimetre of mercury. According to the calculations, this pressure corresponds to the atmospheric pressure at a height of 81.47 English miles above the surface of the earth. As electricity passes with more facility through hydrogen than through air, it would therefore follow from those negative experiments that no electric discharge can take place at that altitude (*Nature*, [5] xxii. p. 33, 1880). On the ground of his experiments, Plücker carries to 9 geographical miles the maximum height above the earth at which auroræ boreales can be produced (*Pogg. Ann.* cxvi. p. 53, 1862). According to the calculations of Loomis, the intense aurora borealis which appeared on the 28th of August 1859 extended to 534, and that which appeared on the 2nd of September following to 495 English miles above the surface of the earth (*American Journal of Science and Arts*, n. s. vol. xxxii. p. 318, 1861). From observations made upon 28 auroræ boreales Professor Newton has calculated that their altitude varied between 33 and 281 English miles, and their mean height above the earth amounted to 130 miles (*Nature*, vol. xxii. p. 291, 1880). The calculation of observations made simultaneously at Berlin and Christiansand (Norway) upon the intensely luminous aurora borealis of Jan. 7, 1831, permitted Hansteen to estimate its height above the earth's surface at 26 geographical miles (*J. Müller, Lehrbuch der kosmischen Physik*, Brunswick, 1861). That the aurora in question, seen at Upsal with its crown in the magnetic zenith (*Pogg. Ann.* xxii.), must have presented a considerable height above the earth, appears to follow from the fact that it was simultaneously visible at Madrid (*Verzeichniss beobachteter Nordlichter*, von Fritz, Vienna, 1873). Lemström (*Öfvers. kongl. Vetensk.-Akad. Förhandl.* 1869), however, has shown that auroral rays may also appear, principally in the polar regions, at a small distance above the surface of the earth.



moreover, in experimenting, various circumstances present themselves which act in a perturbing manner upon the experiments, and of which the consequences are difficult to calculate. It will therefore be worth while to attempt to obtain, by a synoptic account and the discussion of the researches already made, some bases for the correct appreciation of this important question.

## § 2.

Walsh took a glass tube bent into an arc in the middle so that the two branches were parallel; this he filled with mercury and placed it vertically with the arc uniting the two branches above, each branch dipping in an insulated cistern filled with mercury. The mercury in the tubes then sank, forming a vacuum of several feet length between the vertical columns of mercury. When one of the cisterns was then charged with electricity, this passed with a violet light through the arc-shaped vacuum, and the mercury in the other cistern showed itself electric. On the other hand, when the mercury was carefully boiled in the tube in order to expel all traces of gas or humidity, the luminous appearance was not presented, and the mercury in the second vessel showed no trace of electricity. Thus the vacuum freed from air and moisture showed itself perfectly insulating. The experiment took place in the presence of Franklin, Smeaton, de Luis, and several other men of science\*.

Morgan made an experiment for the same purpose, although he proceeded differently. He filled with mercury a glass tube, which he placed vertically in a cistern filled with the same metal. This cistern could be closed hermetically by means of a metal plate, and the air above the mercury removed by an air-pump. When this was done the mercury of the vertical tube descended, leaving a vacuum behind it. The upper extremity of the tube was covered over outside by a piece of tinfoil. When the foil received electricity from the conductor of an electrical machine, the interior of the tube became also electric by induction; and this electricity passed, with a green and violet light, through the vacuum and the column of mercury to the cistern: this took place when the tube had been filled with mercury without taking special precautions; but when the latter had been carefully boiled, the vacuum obtained appeared to be insulating†.

For the investigation of the resistance of a vacuum Paul Ermann made use of an ordinary cistern-barometer in which

\* Gilbert's 'Annals,' vol. ii. p. 161.

† Phil. Trans. 1785.

the mercury had been carefully boiled, and the vacuum was put into electric communication with the exterior by a platinum wire soldered to the glass in the upper extremity of the tube\*. The mercury-cistern was connected with a sensitive electroscope. When the platinum wire was electrified the electroscope showed no trace of electricity. Thus the Torricellian vacuum appeared here likewise to be a nonconductor of electricity. Davy obtained the same result with a similar experiment, in which two fine, very light threads were fixed to a platinum wire soldered to the tube. When the electricity was communicated to this, the fine threads diverged and maintained the divergence without modification, while if the vacuum had been a conductor they must have put themselves into contact again†. E. Becquerel made a similar experiment, which led to the same results‡.

Masson employed for his experiments the Torricellian vacuum of a barometer in which the mercury had been carefully boiled§. Two platinum wires were soldered to the part of the tube surrounding the vacuum. Masson tried in vain to produce a discharge between these wires by means of a Ruhmkorff induction-apparatus set in action by a powerful battery; and he infers from this experiment that an absolute vacuum must be considered an electric nonconductor. Some very just remarks were made by Gaugain|| in opposition to the results of a more recent experiment¶, in which Masson succeeded in passing the current of a powerful Ruhmkorff induction-apparatus through the Torricellian vacuum.

Some mercurial vapour always remains in the Torricellian space above the column of mercury; it is therefore not an absolute vacuum. To obtain a more complete one, Gassiot\*\* proceeded as follows:—Through a glass tube furnished with platinum wires at its extremities, into which a certain quantity of potass had been introduced, he passed a current of pure carbonic acid until it could be assumed that all the air had been expelled; then the carbonic acid was rarefied by means of an air-pump, and the tube was closed. Connecting now the two platinum wires with the two poles of a powerful induction-apparatus, a continual transformation of the electrical luminous appearance presented itself as the carbonic acid was

\* Gilbert's 'Annals,' xi. p. 164; Riess, *Die Lehre von der Reibungs-electricität*, i. p. 39.

† Phil. Trans. 1822; Riess, *l. c.* p. 42.

‡ Mascart, *Traité de l'électricité statique*, ii. p. 100.

§ *Ann. de Chim. et de Physique* (3) xxxi. pp. 312-315.

|| *Comptes Rendus*, xli. p. 152.

¶ *Ibid.* xxxvi. p. 255.

\*\* Mascart, *Traité de l'électricité statique*, ii. p. 101.

more and more absorbed by the potass. At last, when all the carbonic acid had disappeared, the electricity could no longer pass through the vacuum between the platinum wires. If a galvanometer was then introduced into the circuit, it did not show the slightest deflection.

Gassiot here calls attention to a fact which appears to us to possess a certain importance:—When the gas was so strongly rarefied that the direct discharge ceased to take place, it was nevertheless possible to render the tube luminous by influence. It was sufficient for this purpose to put one of the poles of the induction-coil into communication with one of the electrodes of the tube and connect the other with a strip of tinfoil fixed to the outside of the tube, or, again, to put the two poles each into communication with a special strip of tinfoil fixed to the outside of the tube. Then the current coming from the induction-apparatus could not develop itself, and acted only by induction upon the vacuum. Although the latter was sufficiently complete to prevent the direct current from passing from the induction-apparatus, it was nevertheless possible to produce a current in it by induction.

Gaugain did not succeed in making the current of a Ruhmkorff induction-apparatus traverse a perfect Torricellian vacuum\*; but at the same time he makes another observation which appears to us to be of great importance. If a strip of tinfoil be inserted between the electrodes of a less complete vacuum perpendicularly to the path of the current, the electric light shows, by its colour, that the side of the foil turned towards the positive electrode forms a negative pole, and that turned towards the negative electrode a positive pole. If one of the electrodes be then brought sufficiently near to the tinfoil, the current pierces the latter with a fine hole, through which it afterwards takes its path *exclusively*, which puts an end to the polarity of the foil. This fact proves, according to Gaugain, that the tinfoil does not act here solely as a simple conductor of electricity; for, if that were the case, the greater part of the current would pass through the tinfoil itself, which must rightly be regarded as a better conductor than the rarefied gas which fills the aperture. Gaugain draws from this the conclusion that there must exist at the surface between the metal and the gas a special resistance (we would add, or a contrary electromotive force) opposing the passage of the current through the metal.

Plücker† has also made an observation which throws a bright light upon the point which now occupies us. In some

\* *Comptes Rendus*, xli. p. 152.

† Pogg. *Ann.* cv. p. 70; cf. vol. civ. p. 629.

Geissler tubes furnished with platinum electrodes which had been soldered to them, tubes from which the air had been expelled as completely as possible, the current of a Ruhmkorff induction-apparatus passed at first with a whitish light. In the continuation of the experiment, however, the discharge soon became intermittent, to cease totally at the end of a few minutes. Plücker attributes the cause of this phenomenon to the circumstance that the oxygen of the insignificant quantity of air which was still present in the tube was absorbed by the platinum electrodes, after which the nitrogen remaining was unable to transmit the discharge. If now strips of tinfoil were placed round the tube near its two extremities, but insulated from the platinum electrodes, and the poles of the induction-apparatus put in contact with the tinfoils, the tube recommenced shining with electric light, indicating that induced currents were thus produced in the vacuum by the charge and discharge of the tinfoils. If after some time the electrodes were connected with the poles of the induction-apparatus, the discharges again passed at first with a whitish light, soon became intermittent, and ended by totally ceasing. Afterwards, on the poles of the apparatus being connected with the tinfoils, the tube was again seen to shine with electric light; and these alternations could be continued *ad libitum*. When the electric light was explored with a magnet, it appeared that the induced current producing it circulated with a to-and-fro movement, as there was every reason to expect. Plücker's experiments consequently show that, if the air of the tube is so rarefied that the current of the induction-apparatus cannot traverse it, it is nevertheless possible to produce, with the same apparatus, induced currents in the rarefied air—that is to say, to set in motion the electric material present there. These experiments therefore entirely confirm the above-mentioned experiments of Gassiot\*.

Lastly, Hittorf† succeeded in producing, by the simultaneous employment of the air-pump and intense heating of the tube, a still more perfect vacuum than that obtained by Gassiot with the aid of pure carbonic acid. Even when the distance between the electrodes amounted to only 2 or 3 millim.,

\* von Waltenhofen deduces from his researches the result that, as is natural, the form of the electrodes influences the limit of rarefaction at which the current ceases to traverse the rarefied gas. He remarks, in consequence, that if it were possible to introduce the current into the rarefied gas without the aid of electrodes, the discharge would take place even when the rarefaction was carried so far that a discharge could not be produced with the aid of the electrodes (Pogg. *Ann.* cxxvi. p. 537).

† Pogg. *Ann.* cxxxvi. p. 201.

it was impossible for the current of the most powerful Ruhmkorff induction-apparatus to leap from one of the electrodes to the other. Instead of this, the current passed from one of the platinum wires to the other along the outside of the tube. We shall, further on, return to Hittorf's very instructive investigation. The experiments we have just mentioned show that, if the air of a glass tube is rarefied beyond a certain limit, it is impossible for the strongest current to pass through it; but the experiments of Gassiot and Plücker prove moreover that, even when the limit of rarefaction is reached, it is possible by induction to excite a current in the rarefied gas. From that time there does not appear to have been any reason for maintaining that it is the lack of conductivity in the rarefied gas that prevents the transmission of the direct current of a discharge, that lack not bringing any obstacle to the development of the assuredly weaker influence-currents. The cause of the dissimilarity of the two currents can hardly be sought elsewhere than in the electrodes, which in some way hinder the passage of the current from them to the rarefied gas or *vice versa*.

The influence-current has not such an obstacle to surmount, seeing that it is formed in the gaseous mass itself and has no need to pass, at any point whatever, from a solid conductor to the gas. This deduction is moreover in accordance with the experiment made by Gaugain with the tinfoil; and we shall have, in the sequel, repeated opportunities of confirming it. Thus the experiments which we have mentioned do not appear to constitute a satisfactory proof of the assumption that highly rarefied gas or an absolute vacuum is by itself a nonconductor of electricity.

### § 3.

We now pass to the researches respecting the electrical resistance of gases at different degrees of density.

According to the researches of M. E. Becquerel, gases under the ordinary pressure of the atmosphere commence to become conductors if they be heated to redness\*. In his experiments he employed an ordinary battery to produce the current. Among the observations which he was able to make in this respect we shall cite two which are of special interest for our subject. He observed that, if the surfaces of the electrodes between which the current passed were of different sizes, the apparent resistance of the gas was greater when the current passed from the larger to the smaller than if it circulated in the opposite direc-

\* *Comptes Rendus*, xxxvii, p. 22; *Traité du magnétisme et de l'électricité*, Paris, 1855.



tion. Therefore, to obtain as small a resistance as possible, as large a surface as possible must be given to the negative pole. It appeared moreover that the material composing the surfaces of the poles had an influence upon the amount of the apparent resistance. These observations have been confirmed by those which we shall cite below, and present the interesting feature that the current was produced by an ordinary battery, which was of course not sufficiently powerful to call forth the formation of a voltaic arc. Hittorf has specially confirmed the fact that gases become conductors when heated to redness\*.

Gaugain† made the following observation :—If the current of a Ruhmkorff apparatus passes through the air in a glass tube in which two platinum wires are inserted as electrodes, a galvanometer intercalated in the circuit shows that the intensity of the current increases in proportion as the air is rarefied, until the rarefaction has reached a certain limit, but that the intensity begins to diminish if the rarefaction be carried beyond that limit. The degree of rarefaction at which the intensity of the current arrives at its maximum depends on a multitude of circumstances—such as the distance between the electrodes, the size of their surfaces, the width of the tube, &c. In general the degree of rarefaction necessary for the maximum of intensity of the current has increased in the same measure as the augmentation of surface of the negative electrode; when, on the contrary, the surface of the latter was small, the rarefaction of the gas did not need to be carried so far in order to bring about the maximum of intensity of the current.

Morren has found in his experiments the observation confirmed that the intensity of the current augments with the rarefaction of the gas up to a certain limit, past which it begins to diminish if the rarefaction is carried further‡. He employed for this purpose a Ruhmkorff apparatus, and a glass tube of 29 millim. internal diameter and 45 centim. length, in which the distance between the soldered aluminium electrodes amounted to 24 centim. Hydrogen commenced giving evident deflections when the rarefaction had reached a pressure of 74 millim. of mercury; the deflections presented themselves at 39 millim. for carbonic acid, at 29 for atmospheric air, and at 23 for nitrogen and oxygen. Of course these figures possess only a relative importance and are of value only for the conditions under which the experiments took place. The maximum intensity of the current presented itself, for the first-mentioned gas, at a pressure of 1 millim., for oxygen and

\* Pogg. *Ann. Jubelband* (1874), p. 434.

† *Comptes Rendus*, xli. p. 152 (1855).

‡ *Ann. de Chimie et de Physique*, (4) iv. p. 325 (1865).

atmospheric air at 0·7, for carbonic acid at 0·8, and for nitrogen at 1 millim. Employing tubes and electrodes of equal size in all his experiments, Morren had not, like Gaugain, the opportunity of observing how the maximum of intensity of the current depended on the width of the tube, as well as on the distance and the size of the electrodes.

Schultz\*, in his researches, employed as source of electricity the Holtz machine instead of the Ruhmkorff apparatus. He also used Faraday's method for the determination of the electric tension necessary upon the electrodes for the production of a discharge at different densities of the enclosed gas. The following were the results of Schultz's researches:—For the passage, through rarefied air, of electricity between electrodes at a determined distance from one another, the tension necessary diminishes with the reduction of the density of the gas, until the rarefaction has reached a certain limit at which the before-mentioned tension acquires its minimum value; if the rarefaction is carried beyond that limit, the electric tension must again increase for a discharge to be possible. The density of the gas at which the tension necessary for the discharge presents its lowest value depends on the width of the tube and the condition of the electrodes. These two conclusions are in conformity with those established by Gaugain and Morren. But Schultz made another important observation, of special interest for our subject: he found that, if the pressure of the gas was greater than that at which the minimum of tension was presented, the tension necessary for the discharge increased, all other circumstances being equal, with the distance between the electrodes; when, on the contrary, the pressure of the gas was inferior, the tension was independent of the distance between the electrodes. This agrees with the observation made by De la Rive, according to which, *cæteris paribus*, the tension is proportional to the distance between the electrodes†. In the experiments made by De la Rive, however, the density of the gases examined (hydrogen and nitrogen) was higher than that at which they possessed their least resistance; he made no experiment at a lower density than that at which the resistance was at its minimum.

‡ G. Wiedemann and Rühlmann executed in conjunction, and afterwards the former alone, some researches on the course of electricity in rarefied gases‡. The source of electricity em-

\* Pogg. *Ann.* cxxxv. p. 249 (1868).

† *Comptes Rendus*, lvi. p. 669; *Arch. d. Sci. Phys. et Nat.* (2) xvii. p. 53; *Mém. de la Soc. de Phys. et d'Hist. Nat. de Genève*, xvii. p. 69 (1863).

‡ Pogg. *Ann.* cxlv. pp. 235, 364, and clviii. pp. 35, 252.

ployed in these two series of investigations was a Holtz machine giving a constant quantity of electricity proportional to the velocity of rotation of the disk. In the first series the rarefied gas was contained in a large receiver made of stout sheet brass, and the discharge took place between spherical electrodes of metal, of course insulated from the brass receiver. For the observation of the electric light the receiver was furnished with two apertures opposite each other and covered with glass. In the second series the electrodes were also spherical, but were placed in balls of glass joined hermetically to a glass tube the length and width of which were varied with the experiments. In all the experiments the discharge appeared discontinuous even when the gas had its maximum of rarefaction; this latter, however, was never carried far enough to surpass that of the minimum of tension necessary for the production of the discharge. The object of the investigation was to determine the electric tension necessary under different circumstances to produce an electric discharge.

With the aid of a rotating mirror and a heliometric apparatus ingeniously arranged by Wiedemann, a more particular description of which would not be in place here, it was possible to determine the time between two successive discharges. The source of electricity being constant, that time was proportional to the electric tension of the electrodes at the commencement of the discharge. The most important results of these experiments for the question which we have set ourselves to elucidate here are the following:—(1) If the flow of electricity to the electrodes is constant, the electric tension necessary at the electrodes for a discharge to take place increases with the pressure of the gas. (2) This tension depends, at equal pressure, on the nature of the gas employed; it is greater for dry air than for hydrogen; but it is independent of the chemical nature of the electrodes\*. (3) The experiments made at a pressure of 25 millim. or above showed that the necessary tension increased as the distance between the nearest points of the electrodes was augmented; still the increase was less than proportionate to the augmentation of the dis-

\* That the tension necessary for the discharge was independent of the chemical nature of the electrodes is in contradiction with Hittorf's experiment of which we shall speak further on. The difference of the result obtained by Wiedemann and Rühlmann is doubtless due to the electrodes in their experiments presenting relatively large surfaces and the pressure of the gas being considerable (13·8 millim. and above). It is known from other experiments that the influence of the electrodes is in the inverse ratio of the magnitude of their surfaces, and that it increases with the rarefaction of the gas.

tance\*. (4) If the positive electrode was put into communication with the earth, the requisite tension was but little greater than when both insulated electrodes were connected with the electrical machine; if, on the contrary, it was the negative electrode that communicated with the earth, a still stronger tension was necessary in order to call forth the discharge.

The authors note, at the end of their first memoir, that the circumstances observed during the electric discharge in rarefied gases appeared to argue the existence of a sort of resistance to the passage at the surface between the electrode and the environing medium, obstructing the issue of the electricity from the electrode.

In the second memoir Wiedemann communicates various observations made with the view of determining the dependence of the tension necessary for the discharge on the length of the glass tube between the glass spheres furnished with electrodes. The minimum of pressure of gas employed in this series of observations was from 0·8 to 9·0 millim., and was consequently considerably lower than in the corresponding series of experiments of the first memoir. As conducted at pressures for the most part lower, the series in question give also as their result that the electric tension appears to be sufficiently independent of the length of the glass tube. For tubes of equal lengths but different widths, uniting the glass spheres, no great difference was shown in the tension of the electrodes necessary to produce the discharge. When the apparatus was filled with rarefied hydrogen, the necessary tension of discharge was less than when it was filled with rarefied air.

Wiedemann also made some experiments to ascertain the quantity of heat evolved, under the prevalence of different conditions in the tube, by the passage of the electricity. In regard to this, he found that, with an equal flow of electricity, the evolution of heat increased with the increase of the density of the gas, and that the amount of heat evolved was, *cæteris paribus*, nearly independent of the width of the tube. On a former occasion Wiedemann had found that, when the current of an induction-apparatus was passed through a Geissler tube, the evolution of heat was proportional rather to the intensity of the current than to the square of this, as would be required by Joule's law for continuous currents and solid or liquid conductors†. These two positions have been completely confirmed by Naccari and Bellati‡, who found, on employing a Ruhm-

\* Pogg. Ann. cxlv. p. 374.

† Ibid. cxlv. p. 237.

‡ Beiblätter zu den Ann. d. Phys. u. Chem. ii. p. 720 (1878).

korff induction-apparatus, that the quantity of heat evolved in a Geissler tube is proportional to the quantity of electricity that has passed through the tube, and is almost independent of the diameter of the tube. The quantity of heat evolved at the negative electrode was in the same way proportional to the quantity of electricity which had passed through the tube, and several times as great as at the positive electrode; at this latter the quantity of heat evolved was so very small that it was impossible to determine distinctly its proportionality to the amount of electricity.

#### § 4.

From the observations above cited we can already deduce some results which will find their confirmation in the observations expounded below. When the electric current passes through rarefied gas, the gas is heated. This could not take place unless the gas opposed an obstacle to the electric motion. The current is forced to consume a certain amount of work to overcome this obstacle; and it is the work consumed that is transformed into heat. We must admit, on the ground of this observation merely, that the gas exerts a resistance to the propagation of the electricity; it is, besides, of no importance whatever for our consideration to know the nature of that resistance, whether it is or is not homogeneous with that which occurs among solid and liquid bodies. The observations above-mentioned show that the quantity of heat evolved may be regarded as proportional to the intensity of the current, and not to the square of that intensity as Joule's law would require it to be. It follows directly from this, that, all other circumstances remaining equal, the amount of heat evolved must be independent of the section of the tube containing the gas.

Suppose, for example, two tubes of equal length, filled with the same gas, the section of one tube being  $n$  times as large as that of the other, and the same current  $s$  passing through both. Then  $\frac{1}{n}$  of the current passes through each  $\frac{1}{n}$  of section of the wide tube, whence it follows that the evolution of heat in each equal part is proportional to  $\frac{s}{n}$ , and consequently that the heat evolved in all the parts united is proportional to  $s$  (that is to say, of an amount equal to that in the narrow tube). Of course, moreover, *ceteris paribus* the evolution must increase with the length of the tube, and be in general proportional to that length. If  $r_1$  denote the specific resistance in a column of gas of unit length, the heat evolved in  $l$  units of length will



be proportional to  $r_1 l s$  when the current  $s$  traverses that column. Now Wiedemann's experiment has demonstrated that the quantity of heat evolved diminishes with the rarefaction of the gas, while the quantity of electricity which has passed is the same, whence it follows that the resistance  $r_1$  of the gas diminishes as the gas is rarefied.

As was said above, according to Wiedemann and Rühlmann the electric discharge in rarefied gases presents phenomena similar to those which would be called forth by the existence of a sort of resistance to the passage of electricity impeding its escape from the electrodes. Gaugain's above-mentioned observation with the tinfoil is in favour of such an admission. If such a resistance between the tinfoil and the surrounding rarefied gas be not admitted, it is impossible to understand why the electricity passes *exclusively* through the aperture, as the metal must be regarded as a better conductor than the gas. We can cite an allied phenomenon well suited to furnish an elucidation in regard to this. When the resistance opposed by the voltaic arc to the propagation of the galvanic current is measured, that resistance is found to be composed of two parts, one of which is independent of the length of the arc, and the other proportional to that length—provided that, by an appropriate modification of the rest of the resistance in the circuit, the intensity of the current is maintained without sensible variation while the length of the arc is diminished or increased. Here, therefore, the resistance can be expressed by  $a + bl$ , where  $a$  and  $b$  are constants, and  $l$  denotes the length of the arc\*. As  $a$  remains always invariable however short the arc be made, this resistance must have its seat upon the electrodes themselves, whether it be shared between the two or be situated exclusively upon one only. Experiment shows, it is true, that the obstacle  $a$  to the propagation of the current is not produced by a resistance in the ordinary sense of the term, but by an electromotive force which diminishes the intensity of the current quite as much as an ordinary resistance of the amount  $a$ . The propagation of the current in the voltaic arc and in a rarefied gas assumes forms so different that it is impossible to deduce *à priori*, from that which takes place in the one case, what must happen in the other. In the arc, particles are torn from one electrode and transported to the other; but a similar transference is not effected in rarefied gas. The intense evolution of heat which was found by Naccari and Bellati in the negative electrode

\* *Öfvers. Kongl. Svenska Vetensk.-Akad. Förhandl.* 1867, p. 95; Pogg. *Ann.* cxxxi. p. 586.

seems nevertheless to show positively that there, in the same way as in the voltaic arc, an obstacle must exist to the propagation of the current. If we designate this obstacle by  $r$ , the total obstruction to the propagation of the current through the rarefied gas from one electrode to the other must consequently be  $=r+r_1l$ ; and it is necessary that the electric tension of the electrodes be able to overcome this sum in order that a discharge may be possible.

According to the observations which have been cited in the preceding pages, the tension necessary for the discharge diminishes as the gas is rarefied, until a certain limit is reached, after which the tension must be augmented for it to be possible to effect the discharge. The degree of rarefaction at which this turning-point is met with is dependent on the distance between the electrodes, the width of the tube, the amount of surface of the negative electrode, and several other circumstances. Now, as, from the preceding,  $r_1$  diminishes constantly with the increase of rarefaction, the fact in question, demonstrated experimentally by several physicists, can only be explained by the first term,  $r$ , increasing with the rarefaction. I consequently assume that the term  $r$  increases when the density of the gas is diminished. In this manner the sum  $r+r_1l$  can reach its minimum at a certain density; and when this takes place, the minimum of electric tension is sufficient to produce the discharge. If a Ruhmkorff induction-apparatus or an ordinary battery endowed with great electromotive force be employed as the source of electricity, the intensity of the current is found to increase as the rarefaction is continued, until the above-mentioned turning-point is reached, after which the intensity begins again to diminish. If the rarefaction be carried far enough,  $r$  will have so increased that no tension will be sufficient to cause electricity to pass. Now this by no means comes, as it has been assumed to come, from excessively rarefied gas being an insulator, but from the resistance  $r$  having become so great. The fact that the degree of rarefaction at which the point in question is met with depends, as Gaugain has observed, on the distance between the electrodes is explained by the above-mentioned expression of the resistance, into which  $l$  enters as a factor.

If the gas has a pressure corresponding with the ordinary barometric pressure,  $r$  is very small in proportion to  $r_1$ , and can be neglected in comparison with the latter term. It is then seen that the tension necessary for the discharge must be proportional to the distance; that is to say, we arrive at the well-known old law of the distance of the discharge. If the pressure be diminished,  $r$  increases, while  $r_1$  decreases; and

then it is found that the tension necessary for the discharge must increase with the distance between the electrodes, but more slowly than proportionally to that distance. If the gas is strongly rarefied,  $r_1$  can be neglected in comparison with  $r$ ; and the tension necessary for the discharge is then independent of the distance between the electrodes. All these deductions are rigorously conformable to the observations cited.

The fact that electricity cannot penetrate an almost complete vacuum depends, then, according to this exposition, on the resistance to its passage between the electrodes and the surrounding medium having risen above a certain limit\*, and has by no means its reason for existence in the circumstance that the resistance, properly so called, of the gas has received, by the rarefaction, an insurmountable value; on the contrary, the resistance of the gas is diminished when its rarefaction is augmented, so that an absolute vacuum is to be regarded as a good conductor. If that is the case, one ought to be able to call forth, without employing electrodes, an electric motion in a vacuum sufficiently complete for it to be impossible to pass a current in it by means of electrodes. This is in reality what Gassiot and Plücker have already done, in their above-mentioned induction experiments with strips of tinfoil pasted to the outer surface of the tubes. Morgan's experiment, however, also mentioned above, might appear to be in contradiction with the fact cited, since it was impossible to that physicist to produce by influence a luminous phenomenon in the most perfect vacuum. But to this it may be objected that the absence of a luminous phenomenon is not a positive proof that no electric motion took place in the vacuum. Morren, in his experiments upon the passing of electricity through rarefied gases, saw that a galvanometer inserted in the circuit gave an evident deflection before it was possible to perceive any electric light in the tube, although the experiment took place in a dark room†. The reason that in Morgan's experiment no electricity passed to the mercury column was simply that there was a resistance to its passage between the mercury and the vacuum.

I have not been able to find a single certain experimental proof that absolute vacuum is a nonconductor; on the contrary, every thing indicates that vacuum is a good conductor

\* I have designated as a resistance the obstacle which the current has to surmount in order to pass from the electrodes to the gas, or *vice versa*; now by that I do not at all mean that the obstacle is due to a resistance in the ordinary meaning of the term, but rather that it is an electromotive force producing in this respect the same effect as an ordinary resistance.

† *Ann. de Chim. et de Phys.* (4) iv. p. 337.

of electricity. It seems to me that, in drawing from the known impossibility of an electric current traversing the most perfect vacuum between two electrodes the conclusion that a vacuum is absolutely nonconducting, the same mistake has been made as when, from the circumstance that the sun rises in the east and sets in the west, it was believed that one might infer that the sun in reality goes round the earth. The first of these conclusions does not appear more certain than the second.

I will now cite some observations furnishing a new support for the correctness of what has just been said.

### § 5.

Hittorf made a great number of very instructive observations on the conductivity of gases\*. In the first series of his researches he employed, as electric source, a powerful Ruhmkorff induction-apparatus; the gas, contained in Geissler tubes of different shapes and sizes, was rarefied by means of a mercury air-pump. The electrodes were mostly composed of aluminium, but sometimes of other metals. The current was measured by a mirror-galvanometer. Of the results obtained we shall mention only those which have a connexion with our subject.

Two cylindrical tubes, equal in width and length, were furnished at their extremities with electrodes of platinum wire of 0.67 millim. thickness. The electrodes were in part encompassed with tubes of glass. The two positive electrodes had each an equal portion of the wire without a glass covering; but one of the negative electrodes presented a free surface 3.87 times as large as that of the other. The distance between the extremities of the electrodes was the same in both tubes. The tubes therefore presented perfect similarity, except that the negative electrode of one had a larger free surface. When they had both been filled with hydrogen and the pressure of the gas was lowered to 1.35 millim. of mercury, they were inserted side by side in the circuit of the induction-apparatus, the current of which traversed them simultaneously; but it appeared that the current of the tube whose negative electrode had the largest free surface was, on an average, 4.25 times as intense as the current of the other. The intensity of the current was therefore not far from proportional to the free surface of the negative electrode. The same result was obtained with carbonic acid and with nitrogen, as also with aluminium electrodes. Therefore, all other circumstances remaining equal,

\* Pogg. *Ann.* cxxxvi. pp. 1, 197 (1868), Jubelb. p. 430 (1874); Wied. *Ann.* vii. p. 553 (1879).

when the pressure of the gas is very slight the resistance is inversely proportional to the surface of the negative electrode.

Two tubes of equal width, and with equal electrodes, between the extremities of which the distances were 12 and 146 millims. respectively, were filled with hydrogen and connected, side by side, with the poles of the induction-apparatus. The current divided itself between the two tubes; and it appeared that the two portions continually approached nearer to equality as the hydrogen was rarefied. When the pressure had fallen to 1.85 millim., the ratio between the intensities was 1.65; as soon as it had fallen to 0.55, the two intensities became perfectly equal, although the distance between the extremities of the electrodes in one of the tubes was twelve times as great as that in the other. Therefore the resistance designated by  $r_1$  in the foregoing decreased with the pressure of the gas, and at a pressure of 0.55 millim.  $r_1 l$  could be neglected comparatively with  $r$ .

On the other hand, other experiments proved that the resistance  $r$  really increases as the gas becomes more rarefied. Two equal ellipsoidal glass vessels were furnished with equal electrodes of aluminium, then filled with hydrogen at a pressure of 1.05 millim., and connected, side by side, with the poles of an induction-apparatus. The two vessels being equal, the current ought to have been shared equally between them; but it was found that, in consequence of a slight difference between the electrodes, the ratio between the respective resistances of the two vessels was 1.17. The pressure of the gas was afterwards diminished by one half in the vessel which had the less resistance; and now it was ascertained that the resistance was thereby so much increased that it became 2.34 times as great as in the vessel in which the pressure was not changed. Consequently, if the two vessels had had exactly the same resistance before the reduction of the pressure in one of them, the resistance would have been raised to  $2.34 \times 1.17 = 2.74$ . If in both vessels the pressure was 0.5 millim. and was afterwards reduced in one to 0.25 millim., the resistance was thereby augmented in that vessel from 1 to 2.59. These experiments were modified in different ways and with different current-intensities; but the result remained nearly the same.

The gas-pressure in these last experiments being only 1.05 millim. or less, according to the foregoing  $r_1 l$  can be neglected in comparison with  $r$ . These last observations consequently prove, as we have had cause to admit for other reasons before-mentioned, that the resistance  $r$  increases as the gas is rarefied. Much importance attaches to Hittorf's observation that the resistance  $r$  depends on the material of which the negative



electrode is composed. When it was aluminium,  $r$  was at least 4 times less than when the same electrode was composed of silver or of platinum, 2.5 times less than when the constituent material was zinc. Aluminium being, of all metals, that which suffers least from the current, while the latter tears silver and platinum without difficulty, Hittorf is inclined to admit that here, as in the voltaic arc and the electric spark, at the surface of the electrodes exists an electromotive force acting in the opposite direction to the discharge.

In order to decide if the diminution of what we designate by  $r_1 l$  proceeds continuously with the decrease of the gas-pressure, or if it ceases at a certain degree of rarefaction, Hittorf carried on the latter till the pressure was, by calculation, only 0.003 millim.; but to this extreme limit  $r_1 l$  continued to diminish with the pressure. Detailed study of the questions relative to the foregoing furnished to Hittorf the result that there exists at the negative electrode an altogether peculiar cause opposing the passage of the electric current from the gas to the surface of the electrode. When the light surrounding this electrode was explored with a magnet, it was ascertained that the current here passed from the gas to the electrode.

In the subsequent researches which he has published, Hittorf substituted for the Ruhmkorff induction-apparatus a galvanic battery of from 400 to 600 cells. These were composed of carbon, amalgamated zinc, and a solution of potassium bichromate and sulphuric acid. With the Holtz machine and Ruhmkorff apparatus the current which passes through the gas is constantly discontinuous; with the battery, on the contrary, the current was always continuous as soon as the resistance of the rheostat inserted in the circuit did not exceed a certain limit. But if the resistance was above that limit, the current of the battery became discontinuous. It was therefore easy to give the current those two forms at pleasure. Hittorf calls attention to the very slight increase of temperature produced by the current in highly rarefied air. When the tube was a little wider, a thin strip of paper enclosed in it did not show a trace of carbonization when the current traversed it producing an intense light. This is in accordance with the result found by E. Wiedemann\*, that a rarefied gas can be rendered luminous by the passage of the current, although the temperature of the gas may be much below 100° C. This has received further confirmation from the observations of Hasselberg†. But while the gas was so little heated by the current,

\* Wied. Ann. vi. p. 298 (1879).

† Mém. de l'Acad. des Sci. de St. Pétersbourg, [7] xxvii. no. 1 (1879).

the negative electrode became intensely incandescent, though the temperature of the positive electrode was much lower. There must therefore be, at the negative electrode, some cause opposing a considerable obstacle to the propagation of the current. Moreover, on employing the battery as the source of electricity the same phenomena were verified as when the Holtz machine or the induction-apparatus was employed—namely, that the tension necessary for the passage of the current diminished when the gas was rarefied, until the rarefaction had reached a certain limit, past which that tension rapidly augmented. In a cylindrical tube of 1 centim. diameter, and with filiform electrodes, the pressure of the air or hydrogen amounted to 0·7–0·5 millim. when the tension necessary for the discharge was at its minimum. With less than 200 cells it was possible, at the rarefaction mentioned, to pass the current through those gases. The increase or the decrease of the distance between the electrodes had little or no influence upon the number of cells necessary for the passage of the current.

### § 6.

It has, then, been proved by direct observations that the resistance, properly so called, in rarefied gas, or  $r_1$ , diminishes constantly with the pressure of the gas till that pressure has fallen to an insignificant fraction of a millimetre, and that during that time  $r$ , which represents the resistance undergone by the current on passing from the gas to the solid electrode, constantly increases in value. The question may now be stated thus:—Does the known fact that the current is incapable of traversing the Torricellian vacuum depend on  $r_1$ , after constantly decreasing simultaneously with the pressure of the gas, suddenly acquiring a very high value when the last molecules of gas are removed? or is it more probable that the resistance  $r$  upon the electrodes continues to increase? Or, in other terms, which of these two magnitudes is it that increases when the highly-rarefied gas passes to absolute vacuum? Without any doubt the correct assumption is that  $r$  continues to increase with the continuation of the rarefaction, and, in doing so, receives so great an augmentation that the current cannot circulate. Only in this manner, too, is it possible to explain the fact that, without electrodes, a current can be called forth, by induction, in a vacuum deprived of gas, while it is impossible for a current to pass there between electrodes. The observations above related lead therefore, in my opinion, to the remarkable result that *vacuum is a conductor of electricity*.

This at the same time annihilates the difficulty of explaining how one heavenly body can exert an electrical action upon

another, as is the case, for instance, between the sun and the earth. The heavenly bodies are in this way in a sphere of mutual action, not only by universal gravitation and by the radiation of light and heat, but also by the electric force. If vacuum is a good conductor of electricity, an electric motion arising or disappearing on one heavenly body, will of necessity excite, by induction in the vacuum, an electric motion which can be propagated to any distance whatever in that good conductor, and in its turn call forth electrical phenomena upon another heavenly body. The inconsistency with the electrical nature of the aurora borealis which has been supposed to be found in its altitude, sometimes very great, above the surface of the earth, loses thereby all its importance. In the last place, the assumption that the presence of ordinary matter is necessary for the propagation of an electric current from one place to another to be possible will have to be abandoned. If it be agreed that it is possible to an electric motion to propagate itself with the greatest facility *in vacuo*, the notion of *conductivity* will be deprived of all physical meaning. The various material bodies produce only a greater or less *resistance* to the propagation of electricity; their effect in this respect is not *active*, but *passive*.

II. *Some Spiral Figures observable in Crystals, illustrating the Relation of their Optic Axes.* By LEWIS WRIGHT\*.

[Plate I.]

THE true relation of the optic axes in uniaxial and biaxial crystals has always been an interesting subject. We know that if the crystals be both polarized and analyzed circularly, and we disregard any dispersion of the axes for various colours, the axis of a uniaxial and *one* of the two axes of a biaxial present ultimately similar phenomena. Here, for example, is the well known system of rings and brushes presented by a plate of calcite (fig. 1). As is well known, if we interpose between the polarizer and the crystal a quarter-wave plate, the black cross disappears, to be replaced by grey nebulous lines (fig. 2), on alternate sides of which the quadrants are dislocated; and if now we interpose a second quarter-wave plate between the crystal and the analyzer, when the latter is either crossed or parallel even these lines disappear, and we get simply a series of circular rings with no break whatever (fig. 3). Let us now take a plate of sugar cut across one of

\* Communicated by the Physical Society, having been read at the Meeting on November 12, 1881.

its two optic axes. This crystal is suitable for our purpose as having scarcely any axial dispersion, so that one of its axes gives sensible circles, which many other biaxials do not. Placing it in the stage, we have a system of rings traversed by a straight brush (fig. 4), which, on interposing the first quarter-wave plate, becomes a grey line, on each side of which the semicircles are dislocated (fig. 5); but now interposing the second quarter-wave plate, we have perfect unbroken circles as before (fig. 6).

Now this might seem to imply that the optic axis of the uniaxial calcite resembled in its character that of a *single* axis of the sugar, or biaxial. It need hardly be said here, that such was not the view taken of the matter by those intellectual giants who chiefly shaped into definite form the theory of double refraction in crystals. Gradually this theory was simplified, until Fresnel finally framed the conception of three elasticities within the crystal in the direction of three rectangular axes. If all three elasticities were equal, there was no double refraction; if only two were equal, there was a single axis of no double refraction in the direction of the third; if all were unequal, there were two such optic axes. In any conceivable case the wave-surface could be calculated or geometrically projected upon this hypothesis; and it is needless to repeat how, after its author had passed away, Sir William Hamilton worked out from his conceptions the remarkable and unforeseen results of conical and cylindrical refraction which were experimentally verified by Dr. Lloyd (also removed from us during the past year). That extraordinary verification of Fresnel's theory, which makes the optic axes mere resultants of three rectangular elasticities, has always been considered to have placed it upon an impregnable basis, and seems only to have left for future experiment the possibility of perhaps some further illustration, which is the sole object of this paper.

For observe that, according to this theory, the optic axis of our calcite would *not* correspond in character with a single axis of the sugar or any other biaxial, but must be regarded as simply a limiting case in which *both* such axes coincide. This is well illustrated by the celebrated experiments of Professor Mitscherlich in gradually applying heat to crystals, especially to a crystal of selenite, and thereby altering by the unequal expansion their respective elasticities.

Of the two axes gradually approaching till they unite into one as the elasticities are gradually equalized, there could be no clearer proof than this old experiment. But it seemed worth while to seek further illustration of one particular point, viz. that the axis of the uniaxial crystal did actually retain or

embrace within itself, in some visible form, optical characteristics of the two axes thus brought, temporarily or permanently, into coincidence. This object seemed most likely to be obtained by the aid of quartz, or some other substance possessing similar properties of rotary polarization. Such substances having, apart from their ordinary doubly-refractive effects, two different *axial* velocities or waves capable of being brought into interference, and the two axes of a biaxial being according to hypothesis dissimilar, one being principal and the other secondary to it, it seemed probable that by proper means the two axes might be made to exert some kind of differential or selective action upon the two sets of waves passing through the rotary substance. I was confirmed in this expectation by the curious double spiral, first noticed by Sir George Airy, as displayed by quartz itself when subjected to circularly polarized light, the cause of which appeared to me to be connected with this very matter, as we shall presently see to be the case. After observing with more care than usual, therefore, the effects of quartz in combination with other crystals in various ways, most of which have been described by various observers, I finally adopted the following arrangement:—We introduce first, next to the polarizer, a quarter-wave plate, then (in the convergent rays) a plate of calcite, and next to this a plate of quartz 5 to  $7\frac{1}{2}$  millim. thick. The result of this arrangement is the system of double spirals, mutually enwrapping each other, now on the screen (fig. 7). This figure only changes in colour, or moves to or from the centre, as the analyzer is rotated—though there are of course only certain complementary positions of the polarizer, related to that of the quarter-wave plate, which produce them. The point to be here observed is the *double* character of the spiral in this uniaxial crystal.

This figure, however, so closely resembled in all but the number of its convolutions the one exhibited by quartz alone, as described by Sir George Airy in the Cambridge Transactions for 1831, that it might possibly be due to the quartz itself in the convergent light; it was necessary to see if there were any differential results with other crystals, and, finally, to see if they remained when any such possible cause for them was removed. A single axis of sugar was therefore next placed in the crystal-stage in place of the calcite; and the result is again before you (fig. 8). Observe that, with this single axis of a biaxial, we no longer have the double spiral, but a single one, corresponding exactly to the supposed relation of which we are in search, and also showing that the figures are not proper to the quartz as such, but to some selec-



tive action of the axes of the other crystals upon the two axial waves of the quartz and their interferences. A single axis of iron sulphate, and this crystal, cut across a single axis of a topaz, gives similar single spirals.

The single axis being thus tested, we place in the stage a biaxial cut across both axes—in this case nitre (fig. 9). The supposed relation still holds good: each axis now has its own distinct spiral, and the two mutually enwrap one another as in the calcite.

The same is true of crystals whose axes include much wider angles; but to show their spirals we must alter our arrangements. Extra convergent lenses are added in a moment; but if we placed a quartz plate in the strongly convergent light we have to employ to bring both axes of such crystals upon the screen together, the rings and spirals proper to the quartz itself, which have not appeared in the very moderate convergence so far used, would now appear so strongly as to overpower and distort those due to the crystals under examination. We also want to ascertain beyond doubt that the effects are not due to any *convergence* of the rays traversing the quartz, but solely to selective action upon the right-handed and left-handed waves traversing it axially. We therefore reverse the combination, placing a large plate of quartz about  $7\frac{1}{2}$  millim. thick next to the polarizing Nicol, in the parallel rays, and removing the quarter-wave plate to a position between the crystal to be examined and the analyzer. Of course, as it is now the analyzer which is related in position to the quarter-wave plate, the spirals only appear in complementary positions; while, on the other hand, when the analyzer is in those positions the polarizer may be completely rotated. Of course, also, we might have adopted this arrangement all along; but I have given the experiments as they were made, in order to show how each successive question was determined.

A multiplicity of crystals would be useless: three of various angles will show the uniformity and gradation of the phenomena. Our former crystal of topaz cut across one axis, being thin enough also for the more convergent arrangement, will show that the single spiral appears precisely as before, the convolutions being simply closer in this strongly convergent light. Next we will take again the small angle of another nitre crystal, cut thin enough to show conspicuous figures in the convergent apparatus (fig. 10). Observe that we can now barely distinguish its two spirals, by their oval contour, from those just now presented by the calcite: they are a little *drawn out*, as it were, precisely as we should expect; and that is all; otherwise the visible elements are manifestly the same

in both. Arragonite (fig. 11), with an angle of  $18\frac{1}{2}$  degrees, shows a spiral of several turns round each axis; but still they finally enwrap each other: and now mica, with an angle in this specimen of  $60^\circ$  or  $70^\circ$  (fig. 12) gives the same phenomena. With the wider separation the spiral round each axis has room to show separately more of the character of the single axis of the sugar; but the two always preserve the same relation, and only crystals which, owing to very powerful dispersion of their axes, fail to show perfect lemniscates in the ordinary way, fail for the same reason to show these figures complete. Here, for instance, is a plate of borax, whose axial dispersion is considerable and peculiar; but as this still leaves the ordinary lemniscate curves tolerably unbroken, we can trace the spirals without difficulty.

That these figures are solely due to differential action upon the interferences of the quartz rotational colours, we shall demonstrate absolutely in a few minutes; meantime we can almost prove it in two ways. First, though all the arrangements remain complete, the spirals disappear or lose their character in monochromatic light; and, secondly, substituting a quartz of opposite rotation, the direction of the spirals is, as you see, reversed.

And now we will project the beautiful experiment of Prof. Mitscherlich, afterwards applying to it this additional method of analysis. There are the two axes arranged vertically; as we apply heat they gradually unite. The crystal is now uniaxial. And now the axes open out again, but horizontally. It is a beautiful demonstration, which never loses its fascination for the student. We now add our arrangements for the spirals. There they are, arranged perpendicularly on the screen. They approach as the crystal is heated, till now we have them as in the calcite. Now they open out again in a horizontal direction, like those of a plate of nitre turned round  $90^\circ$  in its own plane. Observe that all through we have the *double* spiral. We can only get a single one by taking a single axis; while the axis of a uniaxial always preserves what we may call its "twin" character. Thus we have the ocular illustration sought at the commencement, of the precise relation predicated by Fresnel's theory between the axes of uniaxial and biaxial crystals, and that the former class do contain, within their single axis, elements (capable of being made optically visible) of both the axes in the latter class.

We have here also objectively demonstrated the reason of the double spiral, first observed by Mr. Airy, in quartz itself. We see that the quartz, considered as an ordinary uniaxial crystal, owing to its peculiar effects upon plane-polarized light

passing through it axially, is able to *show its own spirals*, which of course are double. They are not seen at all in parallel light; and, on the other hand, if we increase the rings by convergence, the spirals become more definite. Here, for instance, is a rather thin quartz (one of a pair generally used to show Airy's spirals): in this strongly-convergent circularly polarized light, it shows spirals as well defined as did our calcite. A crucial test of this view readily suggests itself. If it be well founded, obviously we can combine the two properties of our quartz artificially, as it were, since many fluids possess the same power of dividing into two opposite circular waves, differently retarded, a plane-polarized ray. If therefore we take a column of such fluid of sufficient length, and any ordinary uniaxial crystal, the one will represent the peculiar axial properties, and the other the ordinary doubly-refractive properties of the quartz; and the two ought to give similar double spirals. In fact an adequate column of fluid ought to replace the quartz successfully in all the foregoing experiments. Our last step, therefore, is to prove that this is the case. I have here a tube of oil of lemons 200 millimetres (8 inches) in length, which we introduce into the parallel-plane-polarized beam in place of the quartz, whose axial properties it now represents. In the crystal-stage we adjust the calcite, which in all except being a negative crystal (and a positive one would be just the same) represents the ordinary doubly-refractive properties. And now introducing the quarter-wave plate between crystal and analyzer, we have the spirals as given by the quartz in all respects. The same effects are produced by other crystals, any slight inferiority being due to the slightly yellowish tint of the fluid, which so far approximates to homogeneous light. Spirit of turpentine is free from this defect; but we could hardly project through a tube of sufficient length.

These phenomena hold good through all the ordinary analogies with, or substitutes for, natural crystals. This round disk of chilled glass, placed in parallel light, which behaves in all other respects like a crystal in convergent light, also gives double spirals like those of the calcite. I have here also an artificial uniaxial crystal formed of crossed mica-films, after Norremberg, and an artificial quartz of mica-films, after Reusch, for both of which I am indebted to my kind friend Mr. Fox, who made them with his own hands. The first gives the calcite spirals with a quarter-wave plate and quartz; the Reusch preparation gives the quartz spirals with the quarter-wave plate alone.

These experiments of course add nothing to the theory of

the matter, and make no such pretension; their whole interest lies in the visible, ocular demonstration they afford of the truth of conclusions long ago worked out by the brilliant mathematical genius of Fresnel. But to the best of my belief they are new; and if it should prove that some other student has been before me, I hope the beauty of the phenomena may excuse my bringing them before you.

III. *On the Connexion between the Atomic Weight and the Chemical and Physical Properties of Elements.* By THOMAS BAYLEY\*.

[Plate II.]

WHEN we arrange the elements in the order of the atomic weights, hydrogen of course comes first. After this there is a considerable interval, corresponding to an increase of six in the atomic weight, before the next element, which is lithium. After lithium the elements follow in this order,—beryllium, boron, carbon, nitrogen, oxygen, fluorine—the rise in atomic weight between each being on an average about two. The next element is sodium, with the atomic weight 23; and after sodium come magnesium, aluminium, silicon, phosphorus, sulphur, chlorine—the average rise in atomic weight being again about two. If we stay to consider the properties of the elements we have so placed in sequence, our attention is soon arrested by some curious circumstances. Excepting hydrogen, separated as it is by so great an interval from all other elements, lithium is the first. Lithium is a metal of the alkalis, which is only another way of saying that it has properties exceedingly like those of the well-known metals potassium and sodium. It is metallic, strongly electropositive, and chemically active, and of low specific gravity; it forms an oxide and salts which are soluble in water, and formed by the union of the metal with the smallest proportions of oxygen, chlorine, or other negative radical, simple or compound, that are found to be capable of reacting chemically. The next element (beryllium), although its atomic weight is greater than that of lithium only by two, has very different properties. It is metallic, electropositive, and chemically active; but its oxide is insoluble in water, and the metal unites with two atoms of chlorine or bromine to form its halogen compounds instead of with one. The succeeding elements have no longer the metallic character, which, however, has not quite disappeared in the case of boron, the next in succession. Carbon

\* Communicated by the Author.

is non-metallic, very stable under ordinary conditions, and its atom-fixing power is four. Oxygen is gaseous, chemically active, but electronegative, and its atomicity is two. Fluorine is in all probability gaseous; it is chemically active, so much so that it has never been isolated, powerfully electronegative; and its atomicity is one. At this point the character of the elements suffers an abrupt change; and the next element (sodium) is a metal of the alkalies, and almost exactly repeats the properties of lithium. After sodium, as after lithium, come six elements, at small intervals of atomic weight; and they repeat the changes and transitions that take place in the elements succeeding lithium. There is, first, magnesium, a metal of the alkaline earths; and then an earth-metal (aluminium), triad like boron. Next comes silicon, analogous in so many respects to carbon, being neither strongly electropositive nor strongly electronegative, and having also an atomicity of four. Then comes sulphur, electronegative, but less so than oxygen, but with analogous properties in many respects. Chlorine (gaseous, electronegative, and a monad) is like fluorine repeated in a modified form; and then again comes an abrupt change, and an alkali metal (potassium) succeeds. Thus we recognize a periodicity in atomic functions corresponding to intervals of seven elements, and to increase of sixteen in atomic weight.

Potassium and the six succeeding elements form another period, but repeat less distinctly the typical characters of the first periods. There is the same transition from alkali metal to alkaline-earth metal (calcium), from low to high atomicity; and from highly positive elements to the elements chromium and manganese, which, although possessed of basylous properties, have also well-marked chlorous characteristics. But it is evident that potassium and the six elements in succession fail to repeat the full periodic change from alkali metal to alkali metal; there is not the complete transition from positive to negative, and again to positive; nor from low atomicity to high, and again to low. The three elements succeeding to manganese form with it and with copper, which they serve to link together, the iron group, which exhibits within itself so many interesting relations of resemblance and difference. Copper has long been held to have strong affinities with sodium; and it is similar, among other things, in being the first of a series of seven exhibiting the periodic change. For although copper is not a monad, like sodium, the atomicity has fallen rapidly from manganese; and although it is not intensely active, like sodium, it is metallic and electropositive, and has no symptoms of chlorosity. Zinc, the next element,



has analogies with magnesium, and the newly-discovered gallium with aluminium; after gallium the metallic tendency grows weaker and the atomicity higher, in arsenic; and the negative monad type culminates once more in bromine. Again there is a break, followed by a metal of the alkalis—rubidium. We thus recognize the completion of the full period; but it is double, and consists (if we omit the intermediate elements iron, cobalt, and nickel) of two series of seven. The increment from lithium to sodium and from sodium to potassium was sixteen; the increment from potassium to rubidium is approximately three times sixteen—viz. 46·4. From rubidium to the next alkali metal (caesium) the increment is 47·5—almost the same as 46·4; and the intermediate elements form a cycle parallel in a remarkable manner with the cycle from potassium to rubidium. Each of these twin cycles is double, consisting of two series of seven united by an intermediate group, consisting in the second case of palladium, rhodium, and ruthenium. The element silver, at the head of the second series of the fourth cycle, has long been classified with copper, and cadmium with zinc; and the resemblances between antimony and arsenic, between tellurium and selenium, and between bromine and iodine, are among the best-known facts in chemistry.

There is no alkali metal known of higher atomic weight than caesium; but there is strong evidence that, just as the third and fourth cycles succeed the first and second, and correspond to increment of atomic weight three times as great, so the third and fourth cycles are succeeded at any rate by a fifth, with increment of atomic weight again three times as great. The fifth cycle is incomplete, as indeed are the third and fourth in a few members; but it seems to consist of four series of seven, united two to two by the metals osmium, iridium, and platinum, which closely resemble palladium, rhodium, and ruthenium.

It will be seen that, while the cyclic change retains its characteristics unimpaired from the lowest to the highest known atomic weight, the series, which in its early form is cyclic, loses its prominent features as the atomic weight progresses. But besides the natural classification into cycles and series, the elements are capable of another mode of grouping. Certain elements have long been seen to have strong points of resemblance and analogy, and have therefore been grouped into natural families. The alkali metals, the metals of the alkaline earths, and the halogens, are the best examples of family groups. A moment's consideration of these typical examples will show that families consist of elements which have corre-

sponding positions in the ascending series: thus the alkali metals are the first members of certain series, the alkaline-earth metals are the second, and the halogens the sixth members.

The systematic grouping into families, in accordance with this conception, is shown in the table (Plate II. fig. 1), and will be seen to be similar to, but not identical with, Mendelejeff's classification.

Family relationships between elements may be of two orders of intimacy. The halogen group, the group of the alkalis and of the alkaline earths, are among the best examples of complete family resemblance; but there are other groups of elements usually arranged in families which have a certain number of points of resemblance, and yet differ in many important respects. For instance, there is the group consisting of hydrogen, lithium, sodium, copper, silver, and gold; the group comprising beryllium, magnesium, zinc, cadmium, and mercury; the group carbon, silicon, tin, and lead; and the group nitrogen, phosphorus, arsenic, antimony, and bismuth. It is evident that in these cases there is less complete resemblance between the various members of the family, than exists in the case of the halogens and the other aforesaid perfect families. A little consideration will show that the resemblances between some of the members of these imperfect subfamilies, as they may be termed, are often merely structural resemblances of the various compounds formed. For example, the lower chlorides of the subfamily sodium, copper, silver, and gold have little more in common than the fact that the metal in each case is monad, and united to one equivalent of chlorine; while the chlorides of the family of elements lithium, sodium, potassium, rubidium, cæsium, have this feature in common, as well as many others which are not common to all the members of the subfamily—as, for example, solubility in water, and stability under great variety of conditions. In short, we may say that the members of a natural family of elements resemble one another in most physical and chemical characteristics; while the members of a subfamily chiefly resemble the members of the family in atomicity, which accounts for the similar structure of their compounds. But the atomicity of an element seems to depend almost entirely upon position in the primary septenary series; and, upon inquiry, we find that in all cases families and their collateral subfamilies are alike in this respect. It may be thought that too much stress should not be laid upon atomicity, a conception coming of late to be thought less rigidly applicable by chemists. But we here employ the notion of atomicity under

circumstances that admit of comparison under equal conditions. Thus we do not compare the highest atomicity of an element with the highest atomicity of another element, or their atomicities in different compounds and under widely different conditions; but we compare the atomicity of the two elements in those cases where they are united to the same elements—that is, if they are of similar character. And we generally compare them in those compounds in which the two constituents are of oppositive properties (positive and negative) and have most completely balanced each other's affinities. And if we take this last consideration always into account, it sometimes follows that the subfamilies are found to have, besides their resemblances, important structural differences, in which case the family relationship may be considered almost to disappear. The sodium, copper, and silver group, in this way considered, betray, besides the structural resemblances of their lower (proto)chlorides, oxides, &c., more important differences in their *normal* (that is, most stable and evenly balanced) compounds. It may be said that, as the atomic weight increases and the cycles become of greater magnitude, natural families differentiate, splitting first into two and then into four branches, the divergence in properties each time becoming greater and the resemblances less distinct. But in each family there is one branch which preserves unimpaired the original main characteristics of the family.

We may now consider what are the causes of this last phenomenon, this maintenance of the original conditions by one branch of a family; but before doing so, we may indicate some circumstances that are very probably connected with the smaller differences between the members of a family or subfamily of elements. We refer to the proportional position of the elements in the series, or, in other words, to the intervals of atomic weight at which the elements of each series occur. Thus, if we represent increment of atomic weight in each series by a line, we shall find that the lines representing the various series are not proportionally divided, analogous elements occurring at unequal distances from the commencement of the line, and the spaces between pairs of analogous elements being disproportionate. These circumstances, it is conceivable, may be connected with irregularities in the properties of the most closely allied elements.

Passing on to consider the conditions that are associated with and, it may be, cause the resemblances between the members of the main branch of a family, we notice that they are all similarly situated in the cycle. We may, for convenience, distinguish the cycles, the series, and their individual



is represented by a symbol expressing its position as regards other elements and its relations to them, whether axial as among the members of a family, or lateral as between adjacent elements in a series or cycle. Up to the present we have recognized the following circumstances to be connected with the properties of an element:—

- (a) Position of sequence in the series,
- (b) Proportionate position in the series,
- (c) Position in the cycle;

and we have seen that elements having the closest family resemblances are most alike in respect of the first and last of these, and most probably in all.

Accompanying the periodic variations in the chemical properties of the elements by means of which they have been so far systematically classified, are variations in their physical properties synonymous with the chemical variations, and so closely coordinated therewith as almost irresistibly to urge the conviction that the two sets of phenomena (the physical and the chemical) are intrinsically due to the same ulterior causes, or stand in the sequence of cause and effect.

The diagram, Pl. II. fig. 2, which is in some respects the same as those published by L. Meyer in *Die moderne Theorien der Chemie*, has been constructed for me by my friend Mr. Worrall: along the horizontal line as ordinate the elements are set out, according to scale, in the order of atomic weights; and the various curves are formed by joining points in the abscissæ corresponding to each element. The main curve on the diagram thus corresponds to the atomic volumes of the elements, obtained by dividing the atomic weight by the density when known. In cases where the density is not known the element has been simply passed by, a straight line being drawn from the preceding to the succeeding element, or from the nearest preceding to the nearest succeeding element of known atomic volume. The effect of this is somewhat to obscure the resemblance in form between the portions of the curve corresponding to the cycles; but it has the advantage of making the diagram entirely a record of known facts. The line of atomic volume is well worthy of attentive study, which will reveal better than any array of words the singular resemblances and points almost of identity in atomic volume between elements resembling each other quite as closely in chemical properties. It will be seen how the alkali metals in every case have the highest atomic volume, and how the metals with the lowest atomic volumes (those occupying the troughs of the curves) are metals with comparatively small affinities for



oxygen, including the iron-copper group, the platinoid groups, and all the noble and semi-noble metals. Thus the easily oxidizable metals are those which have their atoms exposed at large intervals; the semi-noble metals those which have atoms of medium weight at small intervals; and the noble metals those which have heavy atoms at small intervals. The last may be compared to a Macedonian phalanx of large men with shields interlocked; the semi-noble metals to a phalanx of smaller men; and the alkali and alkaline-earth metals to companies of small men in skirmishing order. The melting-points of the elements are no less closely associated with the periodic variations of chemical properties than are the atomic volumes. A glance at the line of melting-points (at the top of the figure) shows the closeness of the connexion. The alkali metals have in every case low melting-points; the alkaline-earth metals melt at considerably higher temperatures; and the melting-point rises still higher in the metals of the earths, until it culminates in those metals which occupy the intermediate position in the cycle and have low atomic volumes. High melting-point, however, is not always associated with low atomic volume; and it is curious how, in the second, third, fourth, and fifth cycles, the curve of melting-points, after attaining its maximum in silicon in the iron group and in the two groups of the platinoid metals, suddenly falls, until the melting-point again becomes very low, the minimum being within the region of moderately low volume (about 15). This depression is succeeded by a moderate rise; and then the melting-point falls to the alkali-metal standard.

The low melting-point of gallium has been considered to be one of the facts which could not have been anticipated by the light of Mendelejeff's conception; and the Russian chemist, who apparently occupied himself more systematically with chemical than with physical considerations, does not seem to have assigned a low melting-point to ekaluminium, although he has subsequently somewhat empirically attempted to assimilate the fact into his system. But gallium, in having a low melting-point accords perfectly with its atomic weight and density and properties in general; it occupies, in fact, the minimum that immediately succeeds the maximum of melting-point, and is analogous to (nitrogen) phosphorus, indium, and mercury in this respect.

The magnetic properties of the elements have been shown by Carnelley to follow the periodic variations (*Chem. News*, vol. xl. no. 1038); and he has stated the law in the following manner:—"Those elements belonging to the even series of Mendelejeff's classification are always paramagnetic, whereas

the elements belonging to the odd series are always diamagnetic." This supposition is evidently true in the first four cycles, as far as the present state of knowledge enables us to verify it. Thus the first cycle is paramagnetic, and the second diamagnetic. The first half of the third cycle is paramagnetic and the second half diamagnetic; and this is the situation in the fourth cycle also. But if the fifth cycle contains four periods of seven elements, excluding platinum, iridium, and osmium, and we know the first four cycles are strictly septenary, then the series containing gold, mercury, thallium, lead, and bismuth is an even series; and yet these are diamagnetic elements. This and other considerations lead to the modification of the law expressing the magnetic relations. The first cycle (a simple cycle of seven elements) is paramagnetic; the second cycle, also simple, is diamagnetic; after this, in the complex cycles, the first half is paramagnetic and the second diamagnetic. The fifth cycle is incompletely known at present; but if subsequent research shows the first half to be paramagnetic and the second half diamagnetic, it will justify the system of semicycles at the expense of the system of odd and even elements of Mendelejeff.

The property possessed by certain metals of giving coloured solutions when associated as bases with colourless acids is strictly periodic; and the law may be stated as follows:—The metals in the first and second cycles form no coloured solutions; in succeeding cycles the metals occupying the position of lowest atomic volume and the elements immediately succeeding them form coloured solutions. Thus in the third cycle the metals from titanium to copper, in the fourth cycle the metals from niobium to palladium, and in the fifth cycle the platinum group gold and tungsten have this property. It is interesting to observe how the power of forming coloured solutions ceases abruptly in the same region of each complex cycle—in the third cycle after copper, in the fourth after palladium, and in the fifth after gold. To be consistent, silver should form coloured solutions; but its solutions are not coloured, and it is not itself a coloured metal. Possibly its solutions are colourless because they correspond to an oxide of the form  $R_2O$ , just as the salts of copper corresponding to  $Cu_2O$  are generally, but not always, colourless. If this is so, salts of silver corresponding to  $AgO$ , whenever they are discovered, may have coloured solutions.

There is one other circumstance with regard to the position of lowest atomic volume worthy of notice; it is the following:—The increments of atomic weight which, starting from hydrogen, successively give the point where the atomic volume is a minimum, are members of the geometric series

$$a, a \times b, a \times b^2, a \times b^3, a \times b^4,$$

where  $a=10$  and  $b=1.67$ ,

$$= \frac{10}{6}.$$

The increments are

$$10, 16.5, 27.9, 46.6, 77.8;$$

and the corresponding atomic weights,

$$11, 27.5, 55.4, 102.0, 179.8.$$

Enough has now been said to indicate the close connexion between the physical properties of elements and the periodic variation; and it has been shown that in the majority of instances the density, the melting-point, (the expansion for heat,) the magnetism, and the behaviour of the solution to transmitted light have definite relations to the atomic weight. This being so, and it being well known that certain other physical properties of substances closely associated with atomic weight (for instance, vapour-density, isomorphism, and specific heat) are extensively used to decide which of the powers of the equivalent of an element is the weight of its atom, it may be worth while to ask whether the general physical properties of an element, and not only certain isolated ones, should not be called in to decide the all-important question of atomic weight. A crucial test of the value of this method is afforded by uranium. This element has the equivalent 60; and its atomic weight was, until lately, taken as 120. But Mendeleeff, for reasons which he states fully, has assigned to it the atomic weight 240. Our knowledge of uranium and its compounds is largely due to Peligot; and he and others have established the following facts regarding it:—

It has high density, 18.4.

It melts only at the heat of a wind-furnace.

It forms strongly coloured solutions, and, according to Verdet, it is magnetic.

If the atomic weight of uranium is 120, it comes where there is no place for it, between tin and antimony; for its volume is 6.5, while the volume of tin is 16.1 and that of antimony 18.2; it has high melting-point, while they melt at comparatively low temperatures; and it forms coloured solutions, while their solutions are colourless. In the same way, if the atomic weight of uranium is 240, the volume is 13 instead of about 30; and it occupies the region of the fifth cycle beyond bismuth, where, unless all analogy fails, we should not expect to find a metal with very high melting-point and coloured solutions. But if the atomic weight of uranium be 180, it conforms with the known properties of the element. The atomic volume is then 10, and the element takes its place

near tungsten and the platinum group, in the region of high melting-point, low atomic volume, and coloured solutions.

The facts known about the specific heat of uranium are, as far as they go, compatible with the atomic weight 180. The specific heat of metallic uranium has not been determined; but the specific heat of the lowest oxide  $\text{Ur}_2\text{O}_3$  ( $\text{Ur}=180$ ) was found by Regnault to be  $\cdot 0619$ . The product of the specific heat of this oxide and the molecular weight is therefore  $25\cdot 25$ ; and if we subtract from this the assumed specific heat  $13\cdot 00$  of the two atoms of uranium and divide the remainder by 3, we arrive at a highly probable value for this heat of the atoms of oxygen, viz.  $4\cdot 08$ . The heat of the oxygen atoms is by a similar process found to be  $3\cdot 93$  in sesquioxide of chromium,  $4\cdot 12$  in tungstic anhydride, and  $4\cdot 04$  in molybdic anhydride.

The following table exhibits the formulæ of the uranium compounds, taking the atomic weight to be respectively 120, 180, 240:—

Ur=120.	Ur=180.	Ur=240.
$\text{UrCl}_2$	$\text{UrCl}_3$	$\text{UrCl}_4$
$\text{UrO}$	$\text{Ur}_2\text{O}_3$	$\text{UrO}_2$
$\text{Ur}_2\text{O}_3$	$\text{Ur}_2\text{O}_{4\frac{1}{2}} (\text{Ur}_2\text{O}_5?)$	$\text{UrO}_3$
$\text{UrOCl}$	$\text{Ur}_2\text{O}_3\text{Cl}_3$	$\text{UrO}_2\text{Cl}_2$
$\text{Ur}_3\text{O}_4$	$\text{UrO}_2$	$\text{Ur}_3\text{O}_8$
$\text{UrO}_2$	$\text{UrO}_3$	$\text{UrO}_4$

Uranium with atomic weight 180 may be regarded as the atom-analogue of chromium,  $\text{Ur}_2\text{O}_3$  being the analogue of  $\text{Cr}_2\text{O}_3$ , and  $\text{UrO}_3$  of  $\text{CrO}_3$ . The fact of the normal oxide of uranium,  $\text{Ur}_2\text{O}_5$ , being a higher oxide than the normal oxide of chromium,  $\text{Cr}_2\text{O}_3$ , is in accordance with the general tendency of atomicity to increase with atomic weight. To the foregoing it may be objected that tungsten has also claims to be taken as the atom-analogue of chromium; and many arguments might be raised on behalf of each element. Whether it is worth while to raise them is an open question. For it must be remembered that atom-analogy is likely to be most perfect in twin cycles, and to be weaker when the cycles are dissimilar. This is evidently so in the first four cycles: an element in the first cycle resembles its atom-analogue in the second more closely than its atom-analogue in the third or fourth cycle; and an element in the third cycle resembles its atom-analogue in the fourth cycle more closely than its atom-analogue in the first or second.

With increase in the complexity of the cycle comes the development of new features and individualities; thus the property of forming coloured solutions appears for the first time in the third cycle. The factor having the greatest influence in determining the properties of an element appears to be

cyclic position, especially among the higher atomic weights. Now, as the cycle increases, the same progression of atomic weight produces less and less change in cyclic position, and consequently less in properties. Comparing the best-known members of the fifth cycle with the best-known members of the third and fourth, we remark that the progression of atomic weight from gold to bismuth is only about 11, while the progression from silver (107·66) to antimony (120) is about 12, and from copper to arsenic 11·9; and this, although the semi-cyclic progression from cæsium to gold, viz. 66, is three times the semicyclic progression from rubidium to silver, viz. 22·4. Therefore, while the dimensions of the fifth cycle are three times those of the fourth, the mean progression of atomic weight between adjacent atoms is about the same; the obvious inference is the presence of three times as many atoms in the fifth cycle: and upon these facts an argument may be founded to prove the fifth cycle to contain six primary series of seven elements. This supposition receives support from the closeness in atomic weight between cerium and lanthanum and between tantalum and tungsten, and also from the number of newly discovered elements, many of them earth metals, waiting to be classified\*.

On the other hand, this equality in atomic progression does not hold good at the extremities of the cycles; and in these positions the atomic progressions are greatest. There is between potassium and calcium a difference of 1, between rubidium and strontium a difference of 2, while the progression from cæsium to barium is 4. Again, small progressions of atomic weight between adjacent elements in a large cycle might, it is conceivable, be insufficient to bring about transition from one full atomic type to another, and might result in the formation of twin or triplet elements not sufficiently different to have separate atom-analogues in the lower cycles. Cerium, lanthanum, and perhaps didymium may thus have common atom-analogues in yttrium, scandium, and aluminium, and uranium and tungsten in molybdenum and chromium. In this way the fifth cycle may have four or even only two internal periodic variations, and yet have more than thirty-one elements. Again, tungsten may be the atom-analogue of manganese and of the unknown element IV. *a* 7. However, these are questions too obscure to be answered in the present state of chemistry, and await the light of further investigation; but this seems clear, that we must expect to find in the fifth cycle developments not to be found in the lower ones.

\* Some of these may form part of a sixth cycle.



IV. *Note on the Electrical Resistance and the Coefficient of Expansion of Incandescent Platinum.* By E. L. NICHOLS, Ph.D. (Göttingen)\*.

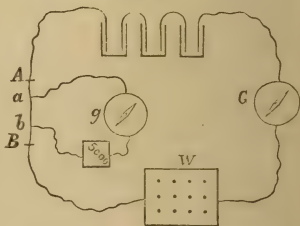
I. **I**N the measurement of temperatures above the red heat, the platinum pyrometer, in one form or another, is as important as the mercury thermometer at ordinary temperatures. The researches already completed, on the electric resistance and the coefficient of expansion of platinum, and on the specific heat of that metal, only serve, however, to remind us of the much that remains to be done before we may hope to attain to even a fair degree of accuracy in the measurement of temperatures above  $500^{\circ}$ .

The present writer, in order to compare the existing formulæ for the temperature of platinum from its electric resistance with those by means of which the temperature is calculated from the coefficient of expansion, and thus to gain a clearer idea of the relative usefulness of the two methods, has determined the resistance and the corresponding length of a platinum wire at various temperatures between  $0^{\circ}$  and the melting-point of that metal.

II. Upon a platinum wire 0.4 millim. in diameter and 100 millim. long, at points 55 millim. apart and equally distant from the middle of the wire, two very fine platinum wires were welded. They served to mark the ends of the portion of the wire to be measured, and to make electrical connexion with a shunt containing a sensitive galvanometer. The wire was heated by the current from a battery of forty Bunsen's cells. Its resistance was determined by the following method.

The wire (A B, fig. 1), together with a tangent-galvanometer (G) and a resistance-box (W), was in direct circuit with the Bunsen's battery. A very small portion of the current was shunted around  $ab$ , the portion of the wire to be tested, and carried through a sensitive sine-galvanometer ( $g$ ) and through a resistance-coil ( $w$ ) of 5000 ohms.

Fig. 1.



\* From Silliman's American Journal for November 1881, having been read at the Cincinnati Meeting of the American Association for the Advancement of Science, August 1881.

Now, with the above arrangement of apparatus, if  $w$  is very much larger than  $r$  (the resistance of the wire  $ab$ ), so that the current through  $ab$  is not sensibly less than that through the main circuit, we shall have

$$E = \frac{C}{r} = \frac{C'}{r'},$$

where  $C$  and  $C'$  are the currents through  $ab$  and through the shunt, and  $r$  is the resistance of the shunt.

But

$$C' = \sin U k',$$

$$C = \tan V k,$$

where  $U$  is the deflection of the sine-galvanometer and  $k'$  the constant of the instrument, and where  $V$  is the deflection of the tangent-galvanometer and  $k$  the constant of the latter instrument.

Then

$$r = \frac{\tan V}{\sin U} \cdot \frac{k}{r'} = \frac{\tan V}{\sin U} \cdot K,$$

where

$$K = \frac{k}{k'} r'.$$

The length of the wire  $ab$  was measured by bringing the two microscopes of a comparator into such position that the terminal  $a$  was in focus in the field of one of the microscopes and  $b$  in the field of the other. Since these points were quite as near the middle as the end of the wire, every change of temperature caused a movement of both  $a$  and  $b$ ; and it was by taking the differences of these that the true change in the length of  $ab$  was determined. As the microscopes were provided with excellent micrometer-scales and screws, a fair degree of accuracy was obtained by this method. Readings of the length of the wire at  $20^\circ$  agreed with a series taken upon a dividing-engine of known accuracy to within  $\cdot 002$  millim. The distance  $ab$  at  $20^\circ$  was found to be  $53\cdot 5576$  millim.

The resistance of the cold wire was found (in terms of  $U$ ,  $V$ , and  $K$ ) by placing the wire in a naphthaline bath, and obtaining values of  $U$  and  $V$  with various amounts of current.

From these readings a curve was drawn with  $\frac{\tan V}{\sin U}$  as abscissæ and  $\tan^2 V$  as ordinates,  $\tan^2 V$  being taken as an expression for the heating effect of the current. The point of this curve corresponding to  $\tan^2 V = 0$  was taken as the proper value of  $\frac{\tan V}{\sin U}$  for the cold wire.

In measuring the resistance of the hot wire, the galvanometers were read simultaneously before and after each determination of the length.

The following table gives the results of the measurements, for temperatures ranging between  $0^{\circ}$  and a point not far below the melting-point of platinum. Both resistance and length of wire at  $0^{\circ}$  are taken equal to unity.

TABLE I.

Resistance.	Length.	Resistance.	Length.
1.0000 .....	1.00000	3.7090 .....	1.01229
1.0410 .....	1.00002	3.7427 .....	1.01223
1.5071 .....	1.00125	3.7813 .....	1.01285
1.9000 .....	1.00289	3.8750 .....	1.01349
2.1212 .....	1.00380	3.8904 .....	1.01371
2.2934 .....	1.00456	3.9305 .....	1.01378
2.3035 .....	1.00489	4.0303 .....	1.01450
2.7821 .....	1.00732	4.0631 .....	1.01469
2.8633 .....	1.00763	4.0655 .....	1.01495
2.9696 .....	1.00809	4.0747 .....	1.01499
3.3533 .....	1.01022	4.0841 .....	1.01514
3.3741 .....	1.01003	4.1248 .....	1.01540
3.4151 .....	1.01042	4.2005 .....	1.01567
3.6449 .....	1.01160	4.2447 .....	1.01632

III. Dr. Siemens has published three formulæ for the variation of the resistance of a platinum wire with the temperature.

The temperatures were calculated in one case (formula *a*) from the heating effect of a copper ball, the specific heat of copper being regarded as a constant; while the other two formulæ were derived from measurements with the air-thermometer.

These formulæ are:—

$$r = .039369 T^{\frac{1}{2}} + .00216407 T - .24127, \quad . \quad . \quad (a)$$

$$r = .0021448 T^{\frac{1}{2}} + .0024187 T + .30425, \quad . \quad . \quad (b)$$

$$r = .092183 T^{\frac{1}{2}} + .00007781 T + .50196, \quad . \quad . \quad (c)$$

where *T* is the absolute temperature and *r* the resistance of the wire. The following formula by Benoit is also sometimes used for the determination of high temperatures:

$$r = 1 + .002445 t + .000000572 t^2. \quad . \quad . \quad . \quad (d)$$

In this expression *t* denotes the temperature in degrees Centigrade.

When, as is frequently the case, it is more convenient to measure the length of a wire than its resistance, we may employ Matthiessen's formula,

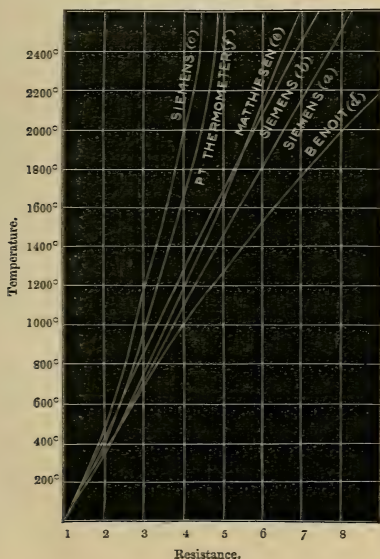
$$l = l_0(1 + \cdot 00000851t + \cdot 0000000035t^2); \quad . \quad . \quad (e)$$

or we may use the uncorrected scale of the platinum thermometer. The latter scale is expressed by the formula

$$l = l_0(1 + \cdot 00000886t). \quad . \quad . \quad . \quad . \quad (f)$$

These being almost the only data we possess for the calculation of the temperature of a hot wire, the question of their accuracy is of some importance. The formulæ may be best compared by plotting side by side the curves which represent them (fig. 2).

Fig. 2.



In fig. 2, resistance is substituted for length in curves *e* and *f*, using for that purpose the measurements given in

Table I. The following table affords a further comparison of the six formulæ.

In the columns *a* to *f* are given the temperatures, calculated by the several formulæ, at which the resistance of the wire, compared with its resistance at 0°, is given in the column marked "*r*."

TABLE II.

Length,	<i>r</i> .	Siemens.			Benoit.	Matthiessen.	Platinum thermo-meter.
		<i>a</i> .	<i>b</i> .	<i>c</i> .	<i>d</i> .	<i>e</i> .	<i>f</i> .
1·0000	1·000	0	0	0	0	0	0
1·0032	2·000	325	402	420	378	342	375
1·0082	3·000	692	812	1108	708	720	917
1·0146	4·000	1086	1244	1950	1000	1170	1623
1·0280	5·000	1464	1682	3170	1272	1638	3100
.....	6·000	1828	2072	.....	1512	2158	
.....	7·000	2170	2387	.....	1766	2800	
.....	8·000	2470	2692	.....	1978		

A glance at the curves and at this table suffices to show how ill-deserved is the confidence generally felt in these formulæ. The discrepancies involve differences of hundreds of degrees.

IV. The methods employed by Dr. Siemens in the measurements represented by curves *b* and *c* were identical; but the platinum used contained slight impurities. To these impurities the disparity was due. Dr. Siemens found that such foreign substances as usually occur in commercial platinum affected both the resistance of the cold metal and the law of the change of resistance with the temperature.

Benoit's formula (*d*) depends for its accuracy upon the determination of the boiling-points of mercury, sulphur, cadmium, and zinc, for which temperatures he adopted the values given by Deville and Troost\*. M. Ed. Becquerel opposed those values at the time of their publication; and later researches have confirmed him, at least so far as cadmium and zinc are concerned, in thinking them to be entirely too high.

In the following table the results obtained by Deville and Troost are compared with the more probable values given by other physicists:—

\* Deville and Troost, *Annales de Chimie*, (3) vol. lviii.



TABLE III.

Metals.	Boiling-points.	Boiling-points.	
	Deville and Troost.	Other values.	
Hg .....	360	350	Regnault. [Journal, 1878]. Bennett (Silliman's American Carnelly and Williams (Quart. Journ. Chem. Soc. 1876-78). Becquerel ( <i>Comp. Rend.</i> lvii.).
S .....	440	{ 448	
Cd .....	860	{ 446 }	
Zn .....	1040	{ 772 } 884	

The substitution of these values in Benoit's formula places it more at variance than before with the measurements of Matthiessen and Siemens—a variation probably due to the difference of behaviour noticed by the latter physicist in the case of different specimens of platinum.

The brief discussion of the above-mentioned results suffices, we think, to show that—

1st. The formulæ in question are based for the most part upon unwarrantable suppositions, such as the constancy of the specific heat of copper and platinum, the constancy of the coefficient of expansion of the latter metal, and upon the accuracy of certain very doubtful values for the boiling-points of zinc, cadmium, &c.

2nd. That, aside from the inaccuracy of those data, the varying resistance of different specimens of platinum renders any formula for the calculation of temperature of that metal from its electric resistance applicable only to the identical wire for which the law of change of resistance with the temperature has been determined.

3rd. That, from the data at command, we are not in position to calculate the temperature of an incandescent platinum wire from its change of resistance, nor from its length, nor indeed in any other manner, further than to express the temperature in terms of the length or the resistance of the wire.

4th. That, owing to the great variations shown by different specimens of platinum as regards its resistance, the determination of the expansion of the wire is to be preferred, whenever practicable, to the measurement of its conductivity.

V. *New Transformations of Ordinals.* By Sir JAMES COCKLE,  
M.A., F.R.S., F.R.A.S., &c.\*

37. IT follows from my paper in the Number for last September (p. 189) that, when certain conditions are fulfilled, we get new transformations.

38. Before showing this, I give a brief verification† of some of the calculations.

39. We have identically

$$N_2 - L_2 = N - L + \omega(\Omega - 1); \quad . \quad . \quad . \quad (9)$$

and the values of  $B_2$  and  $C_2 + b_2$  are given in art. 20.

40. Art. 17 yields the system

$$\frac{C_2 + b_2}{N_2 - L_2} = \eta_2 = 3 - \frac{B_2}{b_2},$$

which the relation

$$b + 3\omega(\omega + 1) = 0 \quad . \quad . \quad . \quad (10)$$

reduces to

$$-(2\omega + 3) = \eta_2 = -(2\omega + 3).$$

41. But, by  $(3)_2$  and (10),

$$\eta_2 = -\frac{1}{2} \{3 \pm (4\omega + 3)\} = -(2\omega + 3) \text{ or } 2\omega.$$

42. If, therefore, we take the radical positively, all the conditions of art. 17 are fulfilled, and we determine  $\omega$  from (10), thus (see art. 32) obtaining :—

$$\omega = \frac{U}{4} - 1 \text{ or } -\frac{U}{4};$$

$$\eta_2 = -\frac{U}{2} - 1 \text{ or } \frac{U}{2} - 3.$$

43. The other two forms for  $\eta_2$ , viz.  $\frac{U}{2} - 2$  and  $-\frac{U}{2}$ , are improper, and in general irrelevant. If, however,  $\omega = -\frac{3}{4}$ , one of the improper forms may be relevant, and only one. Both cannot be so, because, when  $\omega$  takes a single value, that value is  $-\frac{1}{2}$ .

\* Communicated by the Author.

† To verify art. 10, let  $b=0$ , and take the radical negatively. Then (1), (2), become  $B, C=0$ , and (3) is an identity. But  $B, C=0$  together make  $x^3Xt$  linear in  $x^n$ , while  $b=0$  makes  $x^2Xs$  linear in  $x^n$ ; or, in other words, the terordinal in  $z$  is binomial as it stands. I have verified arts. 19 and 20 by the substitutions

$$A, E=0, 0; 1, 1; -1, -1; 2, 1.$$

44. Using suffixes in conformity with the analogies of art. 17, and determining  $h_2$  and  $k_2$  from (iv)<sub>2</sub> and (v)<sub>2</sub>, we shall have (art. 13),

$$f(D)_2 = (D + a_2 - 1) \{ D^2 + 2(a_2 - 1)D + 3f_2 - a_2(2a_2 - 1) \},$$

$$F(D)_2 = (D + e_2 - 1) \{ D^2 + 2(e_2 - 1)D + 3g_2 - e_2(2e_2 - 1) \},$$

and it only remains to determine  $f_2$  and  $g_2$ .

45. But

$$f_2 = L_2 + a_2^2 - a_2 = L - A^2 + A + a_2^2 - a_2,$$

$$g_2 = N_2 + e_2^2 - e_2 = N - E^2 + E + e_2^2 - e_2.$$

46. Now (art. 21) we have four sets of relations; and for the first (art. 22) we get

$$f_2 = 4L + a_2^2 - a_2, \quad g_2 = 4N + e_2^2 - e_2;$$

for the second and third sets respectively (arts. 34 and 35)

$$f_2 = 4L + a_2^2 - a_2, \quad g_2 = N + (e_2 - \frac{1}{2})^2,$$

and

$$f_2 = L + (a_2 - \frac{1}{2})^2, \quad g_2 = 4N + e_2^2 - e_2;$$

and for the fourth (art. 36),

$$f_2 = L + (a_2 - \frac{1}{2})^2, \quad g_2 = N + (e_2 - \frac{1}{2})^2.$$

47. The quadratic factor of  $f(D)_2$  can be written

$$(D + a_2 - 1)^2 - (3a_2^2 - 3a_2 + 1 - 3f_2),$$

which for the first and second sets is

$$(D + a_2 - 1)^2 - (1 - 12L), = (D + a_2 - 1)^2 - (\frac{3}{2}I)^2,$$

while for the third and fourth it is

$$(D + a_2 - 1)^2 - (\frac{1}{4} - 3L), = (D + a_2 - 1)^2 - (\frac{3}{4}I)^2;$$

and there are corresponding results for  $F(D)_2$ ,  $e_2$ ,  $N$ , and  $J$ .

48. The relation characteristic of the first set has (art. 33) been given. That for the second is obtained thus:

$$\frac{1}{4} - 3L = (A - \frac{1}{2})^2 = \omega^2, \text{ or } \frac{9}{16} - \frac{3}{4}l = \omega^2;$$

whence (arts. 29 to 32)

$$\frac{9}{16}I^2 = \omega^2 = \left(\frac{U}{4} - 1\right)^2 \text{ or } \left(\frac{U}{4}\right)^2,$$

and

$$U \pm 3I = 0, \text{ or } 4.$$

49. The corresponding relations for the third and fourth sets are:—

$$U \pm 3J = 0 \text{ or } 4; \quad U = 0 \text{ or } 4.$$

50. We may state all our results concisely as follows:—  
When I, U, J are connected by one of the relations

$$U - 3(1 - 0^{2-m})I + 3(1 - 0^{2-n})J = 4, \quad . \quad . \quad (11)$$

$$U + 3(1 - 0^{2-m})I - 3(1 - 0^{2-n})J = 0, \quad . \quad . \quad (12)$$

the terordinal in  $z$  can be transformed into

$$u + \frac{\left(D + e_2 - 1 + \frac{3}{2^n}J\right)(D + e_2 - 1)\left(D + e_2 - 1 - \frac{3}{2^n}I\right)}{\left(D + a_2 - 1 + \frac{3}{2^m}I\right)(D + a_2 - 1)\left(D + a_2 - 1 - \frac{3}{2^m}J\right)} x^3 u = 0 \quad . \quad . \quad . \quad (13)$$

wherein, for the first set  $m=1=n$ ; for the second,  $m=1, n=2$ ; for the third,  $m=2, n=1$ ; and for the fourth,  $m=2=n$ .

51. Both I and J are independently bisignal; and, without affecting I or J, we can change U into  $U \pm 4k$ , where  $k$  is an integer. The restriction in art. 35 disappears.

52. When any one of the conditions implied in (11) or (12) is satisfied, Boole's algorithm would enable us at once to form a terordinal having its factors, as well in the numerator as in the denominator, in arithmetical progression. But (13) yields as many results again; for, since  $a_2 - e_2$  has two values, (13) has two forms.

53. Take  $U=0$ . Here  $\eta_2 = -1$  or  $-3$ . The result yielded by  $-3$  may be always transformed\* into that obtained by Boole's algorithm; not so that yielded by  $-1$ , which is peculiar to the criticoidal transformation.

2 Sandringham Gardens, Ealing near  
London W., December 15, 1881.

*Errata in Vol. XII. (additional).*

- Page 189, art. 2, line 2, first term, for  $d^2$  read  $d^3$   
 „ 190, last line of text, for  $b$  read  $-b$   
 „ 195, line 2, for  $\omega$  read  $\omega$   
 „ 196, art. 34, line 3, for L read 3L  
 „ „ „ 5, for N read 3N  
 „ „ art. 36, line 3, for  $-2$  read 0 or 4

---

\* This transformation is direct, viz. effected by Boole's process. The criticoidal transformation is indirect; viz. we connect two terordinals by means of a biordinal. I have applied Boole's algorithm in the 'Messenger of Mathematics' for November 1881 (pp. 109, 110).

VI. *On the Distribution of the Molecular Velocities in Gases.*

By C. CELLÉBIER\*.

THE molecules of a gas are, according to the modern theory, withdrawn from each other's action during almost the whole of their passage, which takes place in this case in straight lines and with a uniform motion. In all that follows, we shall suppose that a homogeneous gaseous mass, everywhere at the same temperature, is contained in an invariable enclosure impermeable to heat. It is then in a permanent state. The molecular velocities, to which a mean value is often attributed, are really unequal, constantly modified by the collisions; and after a certain time the proportion of the molecules possessing a more or less great velocity will no longer change: the aim of this investigation is to determine their law—that is to say, the *final distribution* of the velocities.

The men of science who have occupied themselves with the molecular collisions, among others M. Clausius, have in general likened them to that of two solid, perfectly elastic spheres, equal in mass and radius, at least in the conditions of permanence which we have just mentioned. We shall attribute to the molecules any form whatever, variable from one to another, so as not to exclude the cases in which they are regarded as a grouping of atoms, those in which they are supposed to possess polarity, &c. With this exception, we shall admit the other hypotheses contained in the preceding point of view, and which may be summed up thus:—

1. The sum of the *vires viæ* of translation of two molecules is not altered by the collision;
2. All the masses are equal;
3. The collision may be compared to that of two solid bodies.

It must be remarked that the total *vis viva* of translation in the whole of the gas, measuring the pressure, is permanent; it is equally invariable for each of the small portions into which the mass may be divided; therefore the first hypothesis, like the second, consists in neglecting some irregularities which may present themselves in one direction or the other, and which will but little modify the result sought. Hence, if the hypothesis of solidity be admitted, the laws of the collision for two spheres or two surfaces of any kind will certainly be the known laws—that is to say, that the projection of the velocity of one of the centres of gravity upon the common tangent

\* Translated from the *Bibliothèque Universelle, Archives des Sciences Physiques et Naturelles*, Oct. 15, 1881, t. vi. pp. 337–373.



plane is not altered by the collision; otherwise the sum of the *vires vivæ* of translation would also be so.

In regard to the solidity so far as the collision is concerned, let us remark that the trajectory of one of the centres of gravity is composed of two straight lines joined by a curve corresponding to the period of mutual action. In the case of two springs bending one another this curve has a certain extent; for two solid spheres it is reduced to a point. More precisely, if  $\alpha$  denotes the displacement of the centre of gravity of a molecule during the collision (that is to say, during the sensible action of another molecule), and  $d$  the distance of the two centres at that instant, the condition of solidity consists in  $\alpha$  being imperceptible compared with  $d$ .

This is only a consequence of the gaseous constitution of which we wish to calculate the effect; for this calculation consists in regarding as negligible the ratio  $\frac{\alpha}{d'}$ ,  $d'$  being the mean distance traversed by a molecule between two successive collisions. It is so also for gases strongly compressed; for such was the case in one of the principal experiments from which the nothingness of the internal work has been concluded. Now, if a body in the solid state pass to that of a compressed gas occupying either eight times or twenty-seven times its original volume, the mean interval between two neighbouring molecules is merely doubled or trebled. At the distance of the original interval they certainly act the one upon the other; and it is evident that in the gaseous state they can hardly be displaced the distance  $d$  without collision: therefore  $d$  and  $d'$  are quite of the same order of magnitude; and if  $\frac{\alpha}{d'}$  is negligible, so is  $\frac{\alpha}{d}$ .

It is moreover easy to see, for solid molecules it is true, that the degree of incompressibility of a body serves as a measure for that of its molecules. If two equal masses, divided each into  $n$  parts, collide with great force, the stress borne by one part will be the same as if it had been isolated and received the impact of one part only. If in that case it is sensibly compressed, as much will happen when it forms part of the mass, and this will be compressed in the same proportion.

We shall examine some particular cases of molecular motions before attacking the general question; but first some remarks are necessary in order to avoid repetitions.

(1) The unit of length is supposed to be chosen so that the total volume comprised in the enclosure is the unit, although it be very great. Even when the molecules are divided into

numerous groups, each of them will contain an immense number. The molecules are classed in groups according to the nature of their velocities; the molecules of one and the same group are supposed to be distributed in a sensibly uniform manner throughout the space.

(2) If  $n$  is the number of molecules of a group, the number of those of which the centre of gravity is comprised in a determined volume  $H$  will be  $nH$ , with an imperceptible relative error. Indeed this is equivalent to saying that it is proportional to the volume. Now it is evident that, when the total volume is divided into a great number of equal parts, the number of centres contained in each will be very great, and the ratios between them sensibly equal to unity. There would only be a difference for the proportions contiguous to the side, it not being possible for the centre of a molecule to exist at a distance from this which falls below a certain limit; but this limit being infinitely small in comparison with the total dimensions, the result is not thereby altered.

(3) We shall have to value the total number of collisions, or that of certain collisions, during a period constantly designated by  $t$ ; this is supposed such that there is an immense number of collisions, and yet they affect only an imperceptible fraction of the total number of molecules of one and the same group; also the cases in which during that time one and the same molecule suffers two collisions can be completely neglected, their number being infinitesimal in proportion to the former.

(4) The directions of the velocities will be indicated by drawing parallel to each of them a radius of a fixed sphere, which will be named the *typical sphere*: the point of the surface at which it ends will be the *typical point* of the velocity; any portion of the surface will be called the *typical region* of the velocities whose typical point is on that region—which will serve for distributing them in groups.

#### FIRST DISPOSITION.

*All the centres of gravity of the molecules have one and the same velocity  $\frac{1}{2}V$ , in parallel directions, which we figure vertical; but  $n$  of these molecules are descending, and the others, in number  $n'$ , are ascending.*

Let  $G, G'$  be the centres of gravity of two molecules which collide, and  $O$  their common centre of gravity; this is in the middle of  $GG'$ , and consequently immovable before the collision; it will therefore continue to be so after it in the absence of any extraneous force: consequently, if after the collision  $G, G'$  are in  $P, P'$  and an instant afterwards in  $Q, Q'$ , the triangles  $POQ, P'OQ'$  being equal, the small spaces  $PQ, P'Q'$

passed through will be equal and parallel. It will therefore be the same with the velocities after the collision, which will be besides in the opposite direction. The *vis viva* not having changed, their value will still be  $\frac{1}{2}V$ ; their projection upon the common tangent plane, too, not having changed, the old and the new velocity will have for their bisectrix the normal to that plane.

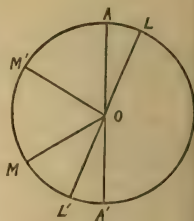
CASE I. *All the molecules are spheres of the same diameter  $\rho$ .*

Let O be the centre of one of the ascending molecules, and let us trace a sphere with centre O and radius  $\rho$ . In order that a molecule of the first kind may come into contact with the sphere during the time  $t$ , its centre G must encounter the surface; and for this it must be, at the commencement of the time  $t$ , interior to the cylinder which would be formed by drawing, through all the points of the upper hemispherical surface, verticals directed upwards and of the length  $Vt$ , since  $V$  is the relative velocity of the two molecules. This cylinder is terminated below by the hemisphere, above by an equal hemisphere; its volume is that of a cylinder of height  $Vt$  and base  $\pi\rho^2$ ; the total volume of the similar cylinders corresponding to all the molecules of the second kind is  $H = n'\pi\rho^2Vt$ ; the number  $\mu$  of centres of molecules of the first kind which are found there at the commencement of the time  $t$  is therefore  $nH$ , according to the second remark above. Hence, putting  $\pi\rho^2 = a$ , results

$$\mu = ann'Vt. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This number, then, is also that of the collisions during the time  $t$ ; for, according to the third remark, the cases in which two descending molecules would have their centres in one and the same cylinder can be omitted, the collision of the one preventing that of the other.

Let us employ the above sphere as typical of the velocities, and draw various meridians through the vertical OA. If the point G (the centre of a descending molecule) meets the surface on one of them in M', the tangent plane common to the two molecules will be parallel to the tangent plane in M', so that, OM being drawn parallel to the new velocity, its typical point M will be upon the same meridian, and the angle AOM double



A O M'. The latter can moreover take all values from 0 to  $\frac{\pi}{2}$ , while the other varies from 0 to  $\pi$ .

Let  $\omega'$  be a surface-element situated in the upper hemisphere, and comprised on the one side between two meridians very near one another and making the angle  $d\phi$ , on the other between two horizontal circles having  $i$  and  $i+di$  for their angular distances from the point A, and consequently  $\rho \sin i$  for radius; we can, as is known, assimilate  $\omega'$  to a small rectangle having for its sides  $\rho di$ ,  $\rho \sin i d\phi$ , and for its surface  $\omega' = \rho^2 \sin i di d\phi$ . The points M corresponding, as above, to all the points M' situated in the area  $\omega'$  evidently constitute an element  $\omega$ , comprised between the same meridians and between two horizontal circles having, for their angular distances from the point A,  $2i$  and  $2(i+di)$ , and therefore for their surfaces

$$\omega = 2\rho^2 \sin 2i \cdot di d\phi, \text{ or } \omega = 4\omega' \cos i.$$

By drawing a vertical of the length  $Vt$  through each point of the area  $\omega'$ , we shall form a very thin prism comprised in the cylinder of which we have spoken, in the interior of which the centre G of a molecule must be in order that the typical point of the velocity due to the collision may be within the element  $\omega$ . Its horizontal section, the plane of which makes the angle  $i$  with the tangent plane in M', will consequently be  $\omega' \cos i$  or  $\frac{\omega}{4}$ .

If now  $\omega$  designates not an element, but a finite portion of the sphere, it can be decomposed into elements such as the preceding; and for the velocity due to the collision to correspond to this new region, the point G must be interior to one or the other of the small prisms corresponding to each element, or, what comes to the same thing, within the second cylinder formed by their union, the section of which is again  $\frac{\omega}{4}$ . Supposing the construction of this second cylinder identically repeated for all the molecules of the second kind, the number  $\mu'$  of the collisions for which the new velocity corresponds to the region  $\omega$  will be the number of the centres G of descending molecules situated in the interior of the second cylinder and of its homologues.

Now  $\mu$  was the number of points G interior to the first cylinder and its homologues;  $\frac{\mu'}{\mu}$  is therefore the ratio of their

volumes or of their sections  $\frac{\omega}{4}$ ,  $\pi\rho^2$ , whence results

$$\mu' = \frac{\omega}{4\pi\rho^2}\mu. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In particular, if it be wished that the acute angle of the new velocity with a given fixed direction LOL' shall be greater than a given acute angle  $\alpha$ , it will be necessary that M be within a zone bounded by two circles whose poles are L, L', and having an angular distance  $\alpha$  from those two points. The height of the zone being  $2\rho \cos \alpha$ , its surface will be  $\omega = 4\pi\rho^2 \cos \alpha$ , and the number of collisions satisfying the preceding condition will be

$$\mu' = \mu \cos \alpha. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Prof. Clausius has remarked that for the new velocities all directions are equally probable. This is what equation (2) expresses, since the number of collisions  $\mu'$  is independent of the position of  $\omega$ . It is this fundamental property that we have now to demonstrate for molecules which are not spherical.

CASE II. *All the molecules of the first kind have any surface S, those of the second kind any surface S'; those of the same sort are not only equal, but similarly oriented; that is to say, the homologous straight lines joining two-points of them are parallel.*

Let us trace apart a typical sphere with centre O, radius 1, for which we will again use the same figure, A being its highest point. If we wish the new velocity of a descending molecule to have M for its typical point, the normal to the plane of the collision must be OM', the bisectrix of OMA. On an ascending molecule S' we shall find the point M'', at which the interior normal is parallel to M'O; there is only one such point, because we shall suppose S, S' convex, without points or sharp edges. We shall displace S by a motion of translation only, so that this surface shall touch S' in M''.

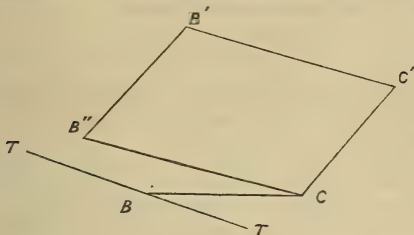
On repeating the operation for all the points M within an infinitely small circle  $\omega$ , the locus of the points M' will be an element  $\omega'$  of the sphere, that of the points M'' an element  $\omega''$  of S', that of the corresponding positions of G a surface-element  $\gamma$  in the space. Carrying through each of these points a vertical of the length  $Vt$ , we shall have formed a thin prism of the volume  $h = \sqrt[3]{t}\gamma \cos i$ ,  $i$  being the angle made by the plane of  $\gamma$  with the horizontal. We will name it the *efficient volume* of the region  $\omega$ , because it is that in which G must be at the commencement of the time  $t$  in order that the new



velocity may correspond to  $\omega$ . We shall thus have

$$\frac{h}{\omega} = Vt \cos i, \quad \frac{\gamma}{\omega''} \frac{\omega''}{\omega'} \frac{\omega'}{\omega}.$$

To simplify this value, let  $B'$ ,  $C'$  denote two points of  $\gamma$  the distance between which is not very small relatively to the dimensions of  $\gamma$ ; let  $B$ ,  $C$  be the corresponding points of  $\omega''$ , and let us draw  $CB''$  equal and parallel to  $B'C'$ . The point



$G$  being at first in  $C'$  the contact was in  $C$ ; a motion of translation bringing  $G$  to  $B'$ , the point of  $S$  which was in  $C$  comes to  $B''$ ; at that instant the contact being in  $B$ , let  $TT$  be the tangent plane common to  $S$  and  $S'$ . The point  $B''$  being upon  $S$ , and  $C$  upon  $S'$ , the distance of each from the tangent plane is, as we know, an infinitesimal of the second order. Therefore the straight line  $CB''$  makes with the plane an infinitely small angle; and it is the same with  $B'C'$ . The same could be said of  $B'D'$ ,  $D'$  being another point of  $\gamma$ . Therefore the plane of  $\gamma$ , in its entirety, is parallel to the plane of  $\omega''$ , and consequently to that of  $\omega'$ .

Next let us call  $M$  specially the centre of the circle  $\omega$ , the points  $M'$ ,  $M''$  being those which correspond to it; it is evident that the ratios  $\frac{\omega'}{\omega}$ ,  $\frac{\omega''}{\omega'}$ ,  $\frac{\gamma}{\omega''}$  do not change if we alter the form of the elements, provided that they exactly correspond to one another and, further, are still at the same place—that is to say, contain  $M$ , or  $M'$ , or  $M''$ ; we have, then,  $\omega = 4\omega' \cos i$ , a relation previously found for a rectangular form. We shall moreover substitute

$$\frac{\omega''}{\omega'} = f(M'), \quad \frac{\gamma}{\omega''} = F(M'', S):$$

the second of these indicates that  $\frac{\gamma}{\omega''}$  depends at the same time on the position of  $M''$  and that of  $S$  relatively to  $S'$ ; and the

first, that  $\frac{\omega''}{\omega}$  depends only on the position of  $M''$  relatively to  $S'$ . It must be remarked that, if while preserving these relative positions we change the general orientation of the figure to make it correspond to another region  $\omega$ , the functions  $f$ ,  $F$  will remain the same.

Lastly, if we name  $H$  the total efficient space  $n'h$  found by combining those of all the molecules of the second kind, we shall get, by the preceding substitutions,

$$\frac{H}{\omega} = \frac{n'Vt}{4} \cdot f(M'') \cdot F(M'', S).$$

(It could be demonstrated that  $f(M'') = RR'$ ,  $R$  and  $R'$  being the principal radii of curvature of the surface  $S'$  at the point  $M''$ .)

CASE III. The data are the same as in the second, except that, for each kind of molecules,  $S$  and  $S'$  can be oriented in all ways, indifferently. It is clear that the equally frequent orientations of  $S$  can be replaced by a numerous series of suitably chosen orientations  $D_1, D_2, D_3$ , &c., the character of which could even be indicated by a differential notation; but it is needless to make a choice as regards the mode of determining them; only they possess the essential property that, if they be all rotated one and the same angle in the same direction about parallel axes, they form an equivalent system of equally frequent orientations. We shall designate by  $D'_1, D'_2, D'_3, \dots$  the analogous orientations for  $S'$ .

The totality of the collisions will be divided into groups by combining those in which the molecules of the first kind have one and the same orientation  $D$ , and those of the second kind one and the same  $D'$ .

The efficient space for a single group is the number  $H$  which we have just found, if  $n'$  be replaced by  $n''$ , the number of molecules of the second kind in the group. Designating now by  $H$  the total efficient volume for all the groups combined, we shall have

$$\frac{H}{\omega} = \frac{Vt}{4} \Sigma' \Sigma n'' f(M'') F(M'', S),$$

the sum  $\Sigma'$  applying to the orientations  $D'_1, D'_2, \dots$ , and  $\Sigma$  to  $D_1, D_2$ , &c. To form the latter, one has to leave the position  $D'$  of  $S'$  invariable, as well as  $M''$ , so that  $f(M'')$  is the common factor; then  $S$  is to be associated with them in the successive positions  $D_1, D_2, \dots$ ,  $n''$  being always the corresponding number of molecules of the second kind: this number is consequently sensibly constant. The positions once

found, if the figure be rotated one and the same angle about one and the same axis carried through  $G'$ , the orientations of  $S$  will again be of equal frequency. Therefore  $\Sigma n''F(M'', S)$  is a function of the same nature as  $f(M'')$ , depending only on the position of  $M''$  upon  $S'$ , and not on the orientation of the latter. We shall therefore have

$$\frac{H}{\omega} = Vt \Sigma' \phi(M''),$$

the function  $\phi(M'')$  being again of the same nature.

The sum will be formed by giving to  $S'$  the positions  $D'_1, D'_2, \dots$  and taking for  $M''$ , each time, the point at which the normal is parallel to  $M'O$ . If we rotate all the positions thus formed one and the same angle about one and the same axis passing through  $G'$ , the normals to the points  $M''$  will again have a common direction, and  $\phi(M'')$  will be the same for each figure; consequently  $\Sigma' \phi(M'')$  will not have changed. The new positions of  $S'$  will again be of equal frequency, and will then all be found to be those which it would be necessary to employ on taking for  $M'$  another point of the sphere, or (which comes to the same) on supposing  $\omega$  at another place. Moreover, as this may be any place whatever, the value of  $H$  is independent of the position of  $\omega$ ; and consequently it is the same with the corresponding number of collisions—which was to be demonstrated.

CASE IV. This will be the general case, in which *the molecules will have any unequal forms whatever*.

We may evidently assimilate them to a numerous series of forms  $F_1, F_2, F_3, \&c.$ , serving as types, and each of which may be oriented in all possible ways. We shall divide the collisions into groups by putting in the same those in which the molecules of the first kind have one and the same figure  $F$ , and the others one and the same,  $F'$ . From what we have just seen, all directions of the new velocities will be equally probable for each group, and therefore also for their union or for all the collisions; and the same property once demonstrated, equation (3), which is the immediate consequence of it, may also be said to be so,  $\mu$  being the total number of the collisions. As to this number, whatever may be the shapes of the molecules, it is proportional to each of the quantities  $n, n', V, t$  separately when it varies alone, the others remaining constant; thus its ratio to  $nn'Vt$  is an absolute constant depending on the nature of the molecules, and which may be designated by  $a$ . Equation (1) is thus verified.

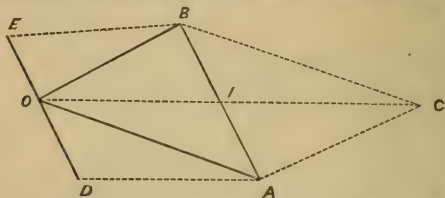
## SECOND DISPOSITION.

The molecules are of two kinds, of which the numbers are  $n$ ,  $n'$ . Those of one and the same kind have equal velocities, parallel and in the same direction, of which the value is  $u$  for the first, and  $v$  for the second; the angle of the velocities is  $\theta$ .

Let us represent these velocities, in magnitude and direction, by  $OA=u$ ,  $OB=v$ ; let  $V$ ,  $V'$  be the diagonals  $AB$ ,  $OC$  of their parallelogram; we shall have

$$V = \sqrt{u^2 + v^2 - 2uv \cos \theta}, \quad V' = \sqrt{u^2 + v^2 + 2uv \cos \theta}. \quad (4)$$

To these let us draw parallels  $DOE$ ,  $AD$ ,  $BE$ .  $OB$  may be regarded as the resultant of two other velocities  $OE$ ,  $OI$ ; in like manner  $OA$  is that of  $OD$ ,  $OI$ . Thus the velocities of



all the molecules are exactly the same as if the entire mass with its boundary had a velocity of translation represented in magnitude and direction by  $OI$  or  $\frac{1}{2}V'$ , while the relative velocities of all the molecules at the commencement of the time  $t$  amounted to  $OD$  for the first species, to  $OE$  for the second. As in the first disposition, these velocities are parallel, in opposite directions, and all equal to  $\frac{1}{2}V$ . Consequently in the relative motion every thing will take place as we have already seen. The total number of the collisions will again be the value of  $\mu$  given in equation (1); besides, designating by  $\theta'$  the acute angle made by one of the new velocities with  $OI$ , there will be, according to equation (3), a number  $\mu \cos \alpha$  of collisions, for which  $\theta' > \alpha$ ,  $\alpha$  being an acute angle chosen arbitrarily.

All these new absolute velocities will be found by compounding the preceding ones with  $OI$  or  $\frac{1}{2}V'$ , which makes the angles  $\theta'$  and  $\pi - \theta'$  with those resulting from one and the same collision. These absolute velocities will therefore be

$$\sqrt{\frac{1}{4}V^2 + \frac{1}{4}V'^2 \pm \frac{1}{2}VV' \cos \theta}$$

It can be verified from formula (4) that the sum of their squares is  $u^2 + v^2$ , as it ought to be, the *vis viva* not having changed.

For brevity let us agree to designate by  $\delta$ , for any collision whatever, the numerical difference of the squares of the new velocities; in the present case we have

$$\delta = VV' \cos \theta', \text{ whence } \delta = \text{or} < VV'.$$

Next, let  $z$  be a given positive number. If the number of collisions for which  $\delta < z$  is required, the answer will be  $\delta = \mu$  if  $z > VV'$ , since the condition is satisfied by all the collisions; but if  $z < VV'$ , on the acute angle  $\alpha$  being chosen so that we have  $VV' \cos \alpha = z$ , the relation  $\delta < z$  gives  $\cos \theta' < \cos \alpha$  or  $\theta' > \alpha$ ; and, as we have seen, the number of collisions sought will be  $\mu \cos \alpha$ , or  $\frac{\mu z}{VV'}$ . On replacing  $z$  by  $z + dz$ , those numbers in the two cases will be  $\mu$  or  $\frac{\mu(z + dz)}{VV'}$ ; taking the difference, we shall have the number  $\mu''$  of collisions for which  $\delta$  is comprised between  $z$  and  $z + dz$ : consequently

$$\mu'' = 0 \text{ if } z > VV'; \quad \mu'' = \frac{\mu dz}{VV'} \text{ if } z < VV'. \quad (5)$$

### THIRD DISPOSITION.

*The molecules are again of two kinds, in number  $n, n'$ ; for each kind the velocities are all equal, viz.  $u$  for the first,  $v$  for the second. For the first kind all are parallel and in the same direction; for the second they are in all directions indifferently. We neglect the collisions occurring between the molecules of the second kind.*

Let us suppose a typical sphere described having for its centre a fixed point  $O$ , and for its radius unity; let us divide it into elements  $\omega$ , and take each of them for the typical region of a group of velocities—that is to say, of the group of molecules of the second kind to which those velocities belong. The velocities being in all directions indifferently, the number of molecules of the group will be  $\frac{n'\omega}{4\pi}$ ,  $4\pi$  being the surface of the sphere. The number of collisions effected between this group and the molecules of the first kind returns into the second disposition, and will be deduced from  $\mu$  by replacing  $n'$  by  $n' \frac{\omega}{4\pi}$ . Putting

$$k = ann't, \quad (6)$$

formula (1) will give  $\mu = \frac{k\omega V}{4\pi}$ ; the number of collisions for which  $\delta$  is comprised between  $z$  and  $z + dz$  will be, according to equations (5),  $\mu'' = 0$  or  $\frac{\mu dz}{VV'}$ , for the single group. Let us



designate this number by  $m'$  for all the groups united, and the total number of collisions by  $m$ ; we shall have

$$m = k \Sigma \frac{\omega}{4\pi} V, \quad m' = k F(u, v) dz, \quad F(u, v) = \Sigma \frac{\omega}{4\pi V'}; \quad (7)$$

the sums are extended to all the elements  $\omega$  of the sphere by suppressing in the second the terms for which the angle  $\theta$  of the velocities would not satisfy the condition  $VV' > z$ . Supposing the radius  $OI$  of the sphere parallel to the velocity  $u$ , we can take for  $\omega$  the narrow zone comprised between two circles having  $I$  for their pole, and  $\theta$  and  $\theta + d\theta$  for their angular distances from that point. Its altitude being  $\sin \theta d\theta$ , we shall have  $\omega = 2\pi \sin \theta d\theta$ ; the angle  $\theta$ , constant throughout its extent, will be that of the velocities;  $V, V'$  will also be the same for the whole of the zone. The sums  $\Sigma$  will become integrals from  $0$  to  $\pi$ . We shall thus have for the indefinite integrals, from the values (7) and (4),

$$m = \frac{1}{2} k \int V \sin \theta d\theta = \frac{k}{6uv} V^3,$$

$$F(u, v) = \frac{1}{2} \int \frac{\sin \theta d\theta}{V'} = -\frac{V'}{2uv}.$$

For  $\theta = \pi$ ,  $V^3 = (u+v)^3$ , for  $\theta = 0$ ,  $V^3 = (u-v)^3$  or  $(v-u)^3$ , according as  $u >$  or  $< v$ . Consequently

$$m = k f(u, v) \quad (8)$$

on putting

$$f(u, v) = u + \frac{v^2}{3u} \text{ if } u > v, \quad f(u, v) = v + \frac{u^2}{3v} \text{ if } v > u. \quad (9)$$

This function is continuous in value, but not in form.

Let us remark next that, from values (4) we get

$$VV' = \sqrt{(u^2 + v^2)^2 - 4u^2v^2 \cos^2 \theta},$$

an expression varying with  $\theta$  between the limits  $u^2 + v^2$  and  $\sqrt{(u^2 - v^2)^2}$ , or the numerical value of  $u^2 - v^2$ .  $z$  must be supposed  $< u^2 + v^2$ , since the collision does not alter the sum of the squares of the velocities.

(1) If, moreover,  $z$  is  $< \sqrt{(u^2 - v^2)^2}$ , the condition  $z < VV'$  being constantly satisfied, in the value of  $F(u, v)$  it will be necessary to integrate from  $\theta = 0$  to  $\theta = \pi$ , which gives

$$F(u, v) = \frac{4}{2uv} [u + v - \sqrt{(u-v)^2}];$$

consequently

$$F(u, v) = \frac{1}{u} \text{ if } u > v; \quad F(u, v) = \frac{1}{v} \text{ if } v > u. \quad (10)$$

(2) But if  $z > \sqrt{(u^2 - v^2)}$ , we shall designate by  $\theta'$  an acute angle such that we have

$$\sqrt{(u^2 + v^2)^2 - 4u^2v^2 \cos^2 \theta'} = z;$$

and it will be necessary to integrate only from  $\theta = \theta'$  to  $\theta = \pi - \theta'$ , between which limits  $VV' > z$ . We thus find

$$F(u, v) = \frac{1}{2uv} [\sqrt{u^2 + v^2 + 2uv \cos \theta'} - \sqrt{u^2 + v^2 - 2uv \cos \theta'}]$$

The factor in brackets having for its square

$$2u^2 + 2v^2 - 2\sqrt{(u^2 + v^2)^2 - 4u^2v^2 \cos^2 \theta'} \text{ or } 2(u^2 + v^2 - z),$$

the result will be

$$F(u, v) = \frac{\sqrt{2(u^2 + v^2 - z)}}{2uv}. \quad . \quad . \quad . \quad (11)$$

Let us now suppose that the number of collisions is required for which one of the new velocities is comprised between two given numbers  $x$  and  $x + dx$  differing very little. The difference  $\delta$  will then lie between two numbers  $z$  and  $z + dz$  corresponding to those; and consequently the number sought will be again the value (7) of  $m'$ . If  $z$  corresponds to  $x$ , the squares of the new velocities being  $x^2$ ,  $u^2 + v^2 - x^2$ , we shall have to suppose  $x^2 < u^2 + v^2$ ; and, moreover,

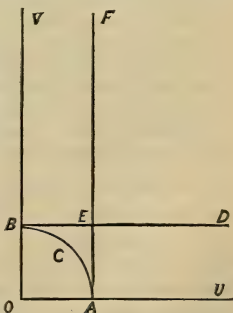
(1) If  $x$  is the greater of the two velocities,  $z = 2x^2 - u^2 - v^2$ ;

(2) If  $x$  is the smaller,  $z = u^2 + v^2 - 2x^2$ .

In both cases it will be necessary to take  $dz = 4x dx$ , the sign — found in the second signifying merely that  $x$  corresponded to  $z + dz$  and  $x + dx$  to  $z$ .

Calling the second velocity  $x'$ ,  $x$  and  $x'$  will both be comprised between  $u$  and  $v$ , or both not comprised, according to whether we have  $z < \text{or} > \sqrt{(u^2 - v^2)^2}$ . Indeed in the first case the difference of the squares of the velocities, which was  $\pm(u^2 - v^2)$ , has become  $z$ , or has diminished; the velocities have therefore come nearer to equality, whilst in the second they have receded from each other. It will therefore be necessary to employ formula (10) in the first case, formula (11) in the second.

The result can be better expressed by regarding  $u$  and  $v$  as rectangular coordinates of a variable point P, referred to the axes OU, OV, the point being in the angle UOV. The quadrant ACB



has  $O$  for its centre,  $x$  for its radius; the straight lines  $AF$ ,  $BD$  are parallel to the axes. We shall then have

$$m' = 4kF(u, v)x \, dx, \quad . \quad . \quad . \quad (12)$$

the function  $F$  of the position of the point denoting:—

(1) If  $P$  is interior to  $OACB$  . .  $F(u, v) = 0$ ;

(2) If  $P$  is in the space  $ACBEA$ , .  $F(u, v) = \frac{\sqrt{u^2 + v^2 - x^2}}{uv}$ ,

(3) If  $P$  is in the space  $FED$ , . .  $F(u, v) = \frac{x}{uv}$ ;

(4) If  $P$  is in the space  $DEAU$ , .  $F(u, v) = \frac{1}{u}$ ;

(5) If  $P$  is in the space  $FEBV$ , .  $F(u, v) = \frac{1}{v}$ .

In fact, for  $OACB$  we have  $u^2 + v^2 < x^2$ , which is impossible. For  $ACBEA$ ,  $u < x$  and  $v < x$ ; for  $FED$ ,  $u > x$  and  $v > x$ ; for both,  $x$  being not comprised between  $u$  and  $v$ , formula (11) is to be employed, substituting in it  $z = 2x^2 - u^2 - v^2$  in the first case (where  $x > x'$ ), and  $z = u^2 + v^2 - 2x^2$  in the second (where  $x < x'$ ).

For  $DEAU$ ,  $u > x$  and  $v < x$ ; for  $FEBV$ ,  $v > x$  and  $u < x$ ; in both cases  $x$  is comprised between  $u$  and  $v$ , and formula (10) is to be employed.

The function  $F(u, v)$  is continuous in value but not in form.

#### FOURTH DISPOSITION.

This differs from the third only in this—that the velocity  $u$ , common to the molecules of the first kind, is in all directions, indifferently, like those of the second; in the same manner, required the number of collisions happening only between molecules of different kinds.

Let us divide the molecules of the first kind into groups of which the velocities correspond to the various elements  $\omega$  of the typical sphere. On reducing the first kind to a single group, we shall be brought back to the third disposition, except that the number  $n$  is to be replaced by  $\frac{n\omega}{4\pi}$ , and the numbers of collisions which were expressed by  $m, m'$ , will now be expressed by  $\frac{m\omega}{4\pi}, \frac{m'\omega}{4\pi}$ ; adding up these values for all the groups, the factors  $m, m'$  remain the same, and we have only to add the values of  $\frac{\omega}{4\pi}$ , which gives the unit. Consequently formulæ

(6), (8), (9), (12) will again give the total number  $m$  of collisions between the molecules of different species, and the number  $m'$  will be that of the collisions at which one of the new velocities is comprised between  $x$  and  $x + dx$ .

#### FIFTH DISPOSITION.

Let us now pass to the real case, in which the velocities are infinitely variable. Let  $N$  be the total number of the molecules of a gas. On making the velocity vary from 0 to infinity by equal small increments, the molecules will be divided into a like number of groups; and we will designate by  $N\phi(x)dx$  the numbers of those whose velocity at the commencement of the time  $t$  is comprised between  $x$  and  $x + dx$ . The collisions against the sides do not alter the velocity; but if the whole of the velocities of all the molecules together be considered, every collision between these has the effect of suppressing two velocities and creating out of them two others. The number of of velocities comprised between  $x$  and  $x + dx$  which are suppressed during the time  $t$  is that of the collisions which have happened between the single group numbering  $N\phi(x)dx$ , on the one hand, and all the groups, on the other. It will therefore be the sum of the values of  $m$ , on replacing therein  $n, n'$  by  $N\phi(x)dx, N\phi(v)dv$ ,  $u$  by  $x$ , and making  $v$  to vary from 0 to infinity. According to formulæ (6) and (8) this sum will be  $N^2at\psi(x)dx$ , putting

$$\psi(x) = \phi(x) \int_0^\infty f(x, v) \phi(v) dv. \quad . \quad . \quad . \quad (13)$$

As to the velocities comprised between  $x$  and  $x + dx$  which are created during the time  $t$ , they may proceed from collisions happening between any two groups whatever, corresponding to the velocities  $u$  and  $u + du, v$  and  $v + dv$ . The number sought will therefore be obtained by replacing in expression (12)  $n$  and  $n'$  by  $N\phi(u)du, N\phi(v)dv$ , then adding those values of the result which correspond to all those of  $u$  and  $v$ . In this way, however, every possible association of two groups will be found to have been reckoned twice; so that half of the sum must be taken. According to formulæ (6) and (12) the number sought will be

$$N^2at\psi'(x)dx,$$

putting

$$\psi'(x) = 2x \int_0^\infty \int_0^\infty F(u, v) \phi(u) \phi(v) du dv. \quad . \quad (14)$$

The number of the velocities comprised between  $x$  and  $x + dx$  will constantly increase or decrease until the instant when an

equal quantity is suppressed and created during the time  $t$ ; this condition, which characterizes the final state, amounts to  $\psi(x) = \psi'(x)$ . The function  $\phi(x)$  is to be determined so as to satisfy the preceding equation for every value of  $x$ .

The unit of length, at first chosen arbitrarily, must now be reduced to one metre. The alteration thence resulting in the formulæ is the same as if we had supposed the enclosure a cubic metre; also, whatever this enclosure may be, it amounts to taking for  $N$  the number of molecules contained in a cubic metre.

### *Accessory Conditions.*

The number of molecules of a group being  $N\phi(x)dx$ , on adding it for all the groups,  $N$  will be found, whence it follows that

$$\int_0^\infty \phi(x)dx = 1. \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Another datum is furnished by the value of the pressure; this for a portion of side  $S$  of 1 square metre has for its value  $p = \Sigma f$ , the summation extending to all the molecules of the medium,  $f$  being for each its normal action upon  $S$ . But, these actions being intermittent, it is preferable to replace it by its mean value during a time  $t$ , this being short enough for the passage of a molecule during it to be inconsiderable in comparison with the dimensions of the enclosure. We thus get

$$p = \frac{1}{t} \Sigma \int_0^t f dt.$$

The quantity  $\int f dt$  does not differ from 0 for a molecule unless it strikes the side during the time  $t$ ; and in that case it measures the impulse given by the side to the molecule—that is,  $2mv$ ,  $v$  being the normal component of its velocity. Consequently

$$p = \frac{2m}{t} \Sigma v,$$

the sum  $\Sigma$  extending to all the impacts against the side  $S$  during the time  $t$ .

CASE I. Let us suppose that all the molecules have velocities  $h$ , equal and parallel, carrying them towards the side, and making with the normal to this an acute angle  $\theta$ . In this case, for a molecule to produce a collision it must at the commencement of the time  $t$  be within a prism having  $S$  for its base,



and its edges of the length  $ht$  parallel to the velocities: its volume being  $ht \cos \theta$ , the number of the molecules included in it is  $Nht \cos \theta$ ; and this is also the number of the collisions. Moreover  $v = h \cos \theta$ , whence results

$$p = 2mNh^2 \cos^2 \theta.$$

CASE II. The molecules have one and the same velocity  $h$ , in all directions, indifferently.

They will be divided into groups, of which the velocities correspond to the various elements  $\omega$  of a typical sphere; and we shall have to replace  $N$  by  $N \frac{\omega}{4\pi}$ , taking for  $\omega$  a thin zone parallel to the side. We shall have, as we have seen,  $\omega = 2\pi \sin \theta d\theta$ ; and on integration from 0 to  $\frac{1}{2}\pi$ , reckoning only the molecules moving towards the side, we get

$$p = mNh^2 \int_0^{\frac{\pi}{2}} \cos^2 \theta \cdot \sin \theta \cdot d\theta = \frac{1}{3} mNh^2;$$

a known formula, often deduced from other considerations, and from which is derived the numerical value of  $h$ .

CASE III. By taking account of the inequalities of velocity, the molecules will be divided into groups. The number of those of one and the same group in the unit of volume is  $N\phi(x)dx$ , which will have to be substituted for  $N$ ; and on adding the result for all the groups, we get

$$p = \frac{1}{3} mN \int_0^{\infty} x^2 \phi(x) dx.$$

Hence results

$$\int_0^{\infty} x^2 \phi(x) dx = h^2. \quad . \quad . \quad . \quad . \quad (16)$$

*Solution of the Equation  $\psi(x) = \psi'(x)$ .*

According to formula (9), the function  $f(u, v)$  having two distinct forms, the integral (13) is to be divided into two others, which gives

$$\phi(x) = \phi(x) \int_0^x \left(x + \frac{v^2}{3x}\right) \phi(v) dv + \phi(x) \int_x^{\infty} \left(v + \frac{x^2}{3v}\right) \phi(v) dv.$$

In the same way, in the value (14) of  $\psi'(x)$ ,  $du dv$  can be regarded as the surface-element of the plane, and the integral can be divided into several others corresponding to the different regions of the figure. According to the values (12) of

$F(u, v)$ , we shall thus get

$$\begin{aligned}\psi'(x) = & 2x \int_0^x dv \int_x^\infty \frac{\phi(u)\phi(v)}{u} du + 2x \int_0^x du \int_x^\infty \frac{\phi(u)\phi(v)}{v} dv \\ & + 2x^2 \int_x^\infty \int_x^\infty \frac{\phi(u)\phi(v)}{uv} du dv + 2x\lambda;\end{aligned}$$

where  $\lambda$  corresponds to the segment ACBE, so that we have

$$\lambda = \int_0^x \frac{\phi(u)du}{u} F'(u), \quad F'(u) = \int_{\sqrt{x^2-u^2}}^x \frac{\sqrt{u^2+v^2-x^2}}{v} \phi(v)dv. \quad (17)$$

The other parts of the value of  $\psi'(x)$ , two of which are equal, decompose into products. Putting

$$\begin{aligned}f &= \int_x^\infty \frac{\phi(v)dv}{v} = \int_x^\infty \frac{\phi(u)du}{u}, & f' &= \int_x^\infty v\phi(v)dv, \\ g &= \int_0^x \phi(v)dv = \int_0^x \phi(u)du, & g' &= \int_0^x v^2\phi(v)dv,\end{aligned}$$

we get

$$\begin{aligned}\psi(x) &= \left[ xg + \frac{1}{3x}g' + f' + \frac{x^2}{3}f \right] \phi(x), \\ \psi'(x) &= 2x\lambda + 4xfg + 2x^2f^2.\end{aligned} \quad (18)$$

The first process which presents itself for finding  $\phi(x)$  consists in assigning to it the form of a series  $a_1x + a_2x^2 + a_3x^3 + \dots$ ; we must then put

$$\begin{aligned}\int_0^\infty \frac{\phi(v)dv}{v} &= k, & f &= k - \int_0^x \frac{\phi(v)dv}{v}; \\ \int_0^\infty v\phi(v)dv &= k', & f' &= k' - \int_0^x v\phi(v)dv.\end{aligned}$$

$\psi(x)$ ,  $\psi'(x)$  will thus contain, besides the constants  $k, k'$ , only finite integrals. The value of  $\lambda$ , on replacing in it for the integration  $u$  and  $v$  by  $u'x, v'x$ , will be expanded into a series, the coefficients containing certain definite integrals easily reducible to one another. It is needless to give the development of this calculation, which is very complicated; it is only necessary to remark that the coefficients  $a_1, a_2, a_3$ , &c. are all expressed as functions of  $k$  and  $k'$ . Consequently, if a function is expansible according to the powers of  $x$ , contains two indeterminate parameters, and, when taken for  $\phi(x)$ , satisfies the equation  $\psi(x) = \psi'(x)$ , that will be the solution, and completely so, especially if it is expansible into

a convergent series for every value of  $x$ . The value of  $\phi(x)$  which satisfies all these conditions is the following:—

$$\phi(x) = \alpha x^2 e^{-\beta x^2}, \quad . \quad . \quad . \quad . \quad . \quad (19)$$

$e$  being the base of the Napierian logarithms,  $\alpha$  and  $\beta$  two positive arbitrary constants. It is expansible into series for all the values of  $x$ ; and, according to what we have just seen, to verify that it satisfies the equation  $\psi(x) = \psi'(x)$  suffices: to suppose  $\alpha = 1$  will be sufficient; the common factor  $\alpha^2$  vanishes everywhere. The values of  $f$  &c. then become

$$g = \int_0^x v^2 e^{-\beta v^2} dv, \quad g' = \int_0^x v^4 e^{-\beta v^2} dv$$

(which cannot be found in a finite form), then

$$f = \int_x^\infty e^{-\beta v^2} v dv = \frac{1}{2\beta} e^{-\beta x^2}, \quad f' = \int_x^\infty e^{-\beta v^2} v dv \times v^2;$$

for  $f'$  the indefinite partial integral is

$$-\frac{v^2}{2\beta} e^{-\beta v^2} + \frac{1}{\beta} \int e^{-\beta v^2} v dv,$$

or between the limits

$$f' = \frac{x^2}{2\beta} e^{-\beta x^2} + \frac{f}{\beta} = \left( \frac{x^2}{2\beta} + \frac{1}{2\beta^2} \right) e^{-\beta x^2}.$$

On substituting these values of  $f, f'$ , formulæ (18) become

$$\psi(x) = x^2 e^{-\beta x^2} \left[ xg + \frac{g'}{3x} + \left( \frac{2x^2}{3\beta} + \frac{1}{2\beta^2} \right) e^{-\beta x^2} \right],$$

$$\psi'(x) = 2x\lambda + \frac{2x}{\beta} e^{-\beta x^2} g + \frac{x^2}{2\beta^2} e^{-2\beta x^2};$$

and on putting

$$e^{\beta x^2} [\psi(x) - \psi'(x)] = \psi''(x),$$

we get

$$\psi''(x) = \left( x^3 - \frac{2x}{\beta} \right) g + \frac{x}{3} g' + \frac{2x^4}{3\beta} e^{-\beta x^2} - 2x\lambda e^{\beta x^2}.$$

Then formula (17) becomes

$$\lambda = \int_0^x u e^{-\beta u^2} F'(u) du, \quad F'(u) = \int_{\sqrt{x^2 - u^2}}^x \sqrt{(u^2 + v^2 - x^2)} e^{-\beta v^2} v dv.$$

Taking for the variable

$$\sqrt{u^2 + v^2 - x^2} = y, \text{ whence } v^2 = x^2 - u^2 + y^2, \quad v dv = y dy,$$

we get

$$F'(u) = e^{\beta(u^2 - x^2)} \int_0^u y^2 dy e^{-\beta y^2}, \quad \lambda = e^{-\beta x^2} \int_0^x u du F''(u),$$

putting

$$F''(u) \int_0^u y^2 dy e^{-\beta y^2}.$$

The indefinite partial integral is

$$\lambda e^{\beta x^2} = \frac{1}{2} u^2 F''(u) - \frac{1}{2} \int u^4 e^{-\beta u^2} du;$$

and between the limits there results

$$\lambda e^{\beta x^2} = \frac{1}{2} x^2 g - \frac{1}{2} g'.$$

On substituting in the above value of  $\psi''(x)$  we have

$$\psi''(x) = \frac{4}{3} x g' - \frac{2x}{\beta} g + \frac{2x^4}{3\beta} e^{-\beta x^2}.$$

Finally, partial indefinite integration gives

$$g' = -\frac{v^3}{2\beta} e^{-\beta v^2} + \frac{3}{2\beta} \int v^2 e^{-\beta v^2} dv,$$

or, between the limits,

$$g' = -\frac{x^3}{2\beta} e^{-\beta x^2} + \frac{3}{2\beta} g,$$

whence results identically

$$\psi''(x) = 0, \text{ and consequently } \psi(x) = \psi'(x).$$

Formula (19) therefore well represents the law of the velocities; and  $\alpha, \beta$  will be found on substituting it in equations (15) and (16), which gives

$$\alpha \int_0^\infty x^2 e^{-\beta x^2} dx = 1, \quad \alpha \int_0^\infty x^4 e^{-\beta x^2} dx = h^2;$$

it will, however, be simpler to employ the number  $h$ , putting

$$h^2 = \frac{3}{2} h'^2, \text{ or } h' = h \sqrt{\frac{2}{3}} = 0.82h,$$

The known integral

$$\int_0^\infty e^{-x^2} dx = \frac{\sqrt{\pi}}{2}$$

gives, on replacing  $x$  by  $x\sqrt{\beta}$  and differentiating twice with respect to  $\beta$ ,

$$\int_0^\infty e^{-\beta x^2} dx = \frac{\sqrt{\pi}}{2\sqrt{\beta}}, \quad \int_0^\infty x^2 e^{-\beta x^2} dx = \frac{\sqrt{\pi}}{4\beta^{\frac{3}{2}}}, \quad \int_0^\infty x^4 e^{-\beta x^2} dx = \frac{3\sqrt{\pi}}{8\beta^{\frac{5}{2}}};$$

the above relations thus become

$$\frac{\alpha\sqrt{\pi}}{4\beta\sqrt{\beta}} = 1, \quad \frac{3\alpha\sqrt{\pi}}{8\beta^2\sqrt{\beta}} = \frac{3}{2} h'^2, \text{ whence } \beta = \frac{1}{h'^2}, \quad \alpha = \frac{\alpha'}{h'^3},$$

if we put

$$\alpha' = \frac{4}{\sqrt{\pi}}.$$

Therefore the law of the velocities is

$$\phi(x) = \frac{\alpha'}{h'^3} x^2 e^{-\frac{x^2}{h'^2}}.$$

The maximum of this expression corresponds to  $x = h'$ . It seems as if the velocities for certain groups might become indefinitely great; but this is only apparent. Indeed, let  $\mu$  be the proportion of the molecules whose velocity exceeds  $nh'$ ,  $n$  being a number containing several units, we shall have, on changing  $x$  into  $h'y$ ,

$$\mu = \int_{nh'}^{\infty} \phi(x) dx = \alpha' \int_n^{\infty} y^2 e^{-y^2} dy,$$

or on partial integration

$$\frac{\mu}{\alpha'} = \frac{1}{2} n e^{-n^2} + \frac{1}{2} \int_n^{\infty} e^{-y^2} dy,$$

or

$$\int_n^{\infty} e^{-y^2} dy = \int_n^{\infty} \frac{1}{y} e^{-y^2} y dy < \int_n^{\infty} \frac{1}{n} e^{-y^2} y dy;$$

consequently

$$\mu < \alpha' \left( \frac{1}{2} n + \frac{1}{2n} \right) e^{-n^2}.$$

For  $n = 10$  or  $x > 8h$ , about, this view of  $\mu$  only commences at the 43rd decimal; and the theory, established for numerous groups, cannot be extended to some singular cases in which only one or two molecules, perhaps, would be concerned. The high velocities can only be brought about by a series of collisions favourably arranged by chance. It is quite otherwise with very low velocities, which a single collision can produce.

The proportion  $\mu'$  of the velocities below a certain value of  $x$  is  $\mu' = \int_0^x \phi(x) dx$ ; and if  $\frac{x}{h'}$  is small, the exponential can be replaced by unity, which gives

$$\mu' = \frac{\alpha'}{h'^3} \int_0^{\infty} x^2 dx = \frac{\alpha'}{3} \left( \frac{x}{h'} \right)^3.$$

For example, the proportion of the velocities below  $\frac{h'}{10}$  is about 0.00075.



VII. *The Beats of Mistuned Consonances.*

By Professor SILVANUS P. THOMPSON, B.A., D.Sc.

*To the Editors of the Philosophical Magazine and Journal.*

GENTLEMEN,

IN a letter published in your December Number Mr. Bosanquet laments that his labours upon the beats of mistuned consonances have been thrown away upon me, because I have ventured to criticise two points in his valuable and interesting researches.

These points are, first, his misuse of the word "subjective" as applied to the phenomena in question; and, second, the priority of Dr. König in the analysis of the phenomenon so far as it can yet be said to be analyzed, to the credit of which Mr. Bosanquet lays a direct claim.

I will deal with Mr. Bosanquet's objections separately, merely observing that it would indeed be a pity if "the credit" of any discovery to which Mr. Bosanquet is entitled could be "taken away by a careless sentence" of mine.

Mr. Bosanquet's attempt to defend his use of the word "subjective," as applied to the difference-tones or beat-notes, is virtually an admission of the very point for which I contend. By way of defence, he retires behind the shelter of Helmholtz and of Mr. Ellis, who, it appears, have lapsed into the same laxity of language. On reading Mr. Bosanquet's reference to Helmholtz, I immediately turned to p. 234 of Ellis's translation (the only edition at hand at the moment), and found that I had underlined the word in pencil, and had added in the margin "*sic*" by way of protest. But whether Mr. Bosanquet sins in good company or not, I am still of opinion that it is unwarrantable to apply the term "subjective" to that which has a physical existence independently of the conscious "ego," or of the brain through which consciousness works. The ear is, as I have said elsewhere, only a complex resonator; and any other suitable resonator will also respond to the tones in question, provided it possesses the asymmetry of its parts which is necessary for the development of those tones. To speak of such tones as subjective is a palpable abuse of the term. But I really do not require to insist further on this point if, as Mr. Bosanquet says, he does not believe "*much*" in the "advancement of clearness by the employment of words very strictly defined."

*Secondly*, as to König's priority in the observation that the beats of imperfect consonances consist of variations in the intensity of the *lower* of the two tones. This observation Mr. Bosanquet says was "unquestionably" first obtained by him-

self. For Mr. Bosanquet's sake I regret that the tone of his letter leaves me no alternative but to produce the evidence upon which I deliberately assigned priority to Dr. König.

Mr. Bosanquet appears to have read König's papers; for he says he "knew" them "intimately," and that "there was no vestige of guidance in them on the subject;" that "König never analyzed his beats, and never enunciated any opinion whatever as to the notes of whose variation the beats consist, except in the one case of the octave . . . where he says that fundamental and octave are heard alternately."

There lie before me at this moment the *Annalen* of Poggen-dorff for the year 1876 (Bd. clvii.) It is true that König states therein that the two primaries are alternately heard; but that he traced this alternation to its true cause is shown by the very paragraph in which this statement occurs. I quote from p. 188 of the volume of the *Annalen*, italicizing the words which Mr. Bosanquet appears to have overlooked when he says that König did not analyze or enunciate any opinion, and that König only touched the case of the octave.

"Eine Eigenthümlichkeit der Stösse harmonischer Intervalle besteht noch darin, das die beiden primären Töne abwechselnd hervortreten. Lässt man neben dem starken, grossen *C* das nur um einen geringen Theil einer Schwingung verstimmt kleine *c* ertönen, so dass sich sehr langsame Stösse bilden, so hört man abwechselnd einmal den Grundton und einmal die Octave so deutlich hervortreten, dass man, wenn das kleine *c* sehr stark ist, mitunter geneigt seyn könnte, jede Schwebung doppelt zu zählen. *Ist das kleine c dagegen schwach, so hört man nur den Grundton abwechselnd stärker und schwächer werden.* Ganz dieselbe Beobachtung habe ich auch bei den sehr langsamen Stössen der *Duodecime*, und der *Doppeloctave*, *C: g* und *C: c'* machen können, aber bei nur einigermaßen schnellen Schwebungen lässt sich das periodische Hervortreten des höheren Tones nicht mehr wahrnehmen."

It is the more remarkable that König's insight into the cause of the alternation mentioned in the first sentence of the paragraph quoted above should have escaped Mr. Bosanquet's notice, since three months before the publication of Mr. Bosanquet's paper in the *Philosophical Magazine* König had published another very important paper in Wiedemann's *Annalen* (Bd. xii. 1881, p. 337), in which the results of a reexamination of the very point in question are most unequivocally laid down. I quote the passage from p. 341, again italicizing the important words.

"Regulirt man ferner die Intensität der beiden Töne eines alternirten harmonischen Intervalls in der Weise, dass die Stösse am deutlichsten hervortreten, so müssten, wenn sie durch den höheren primären Ton und einen im Ohre erzeugten harmonischen Oberton

des tieferen, also durch zwei Töne im Einklang gebildet wären, diese Stösse auch auf diesen Oberton gehört werden, man nimmt aber gerade das Gegentheil wahr, d. h. das *der Grundton seine Intensität periodisch ändert und dabei nur in den Momenten grösster Schwächung den höheren Ton hervortreten lässt, wie ich früher beschrieben.*”

With Mr. Bosanquet's permission, I will translate the words in which Dr. König states what he observes, namely that “*the fundamental tone alters its intensity periodically, and thereby allows the higher tone to come out only in the moments of greatest enfeeblement, as I formerly described.*”

I will leave to your readers to decide whether the alleged injustice of my “careless sentence” is objective or subjective in character; or whether credit for discovery is one of those terms in the strict definition of which we are not to believe “much.”

I remain, Gentlemen,

Yours faithfully.

University College, Bristol,  
December 19th, 1881.

SILVANUS P. THOMPSON.

## VIII. *Proceedings of Learned Societies.*

### GEOLOGICAL SOCIETY.

[Continued from vol. xii. p. 75.]

November 2, 1881.—Robert Etheridge, Esq., F.R.S., President,  
in the Chair.

THE following communications were read:—

1. “On the Genus *Stoliczkaria*, Dunc., and its Distinctness from *Parkeria*, Carp. and Brady.” By Prof. P. Martin Duncan, M.B. Lond., F.R.S., F.G.S., Pres. R.M.S.

2. “On the Elasticity- and Strength-constants of Japanese Rocks.” By Thomas Gray, Esq., B.Sc., F.R.S.E., and John Milne, Esq., F.G.S.

In this paper the authors described the results of some experiments made to determine the elasticity-constants and strength against rupture and crushing of a few of the commoner Japanese rocks, their chief object being to obtain data for calculating the theoretical velocities of earthquake-wave transmission. The rocks submitted to experiment were a grey granite, a pure white crystalline marble, a greyish-green soft tuff, a mottled clay-rock, and clay-slate.

Young's moduli were determined by the bending of solid cylinders of the rocks in an apparatus described and figured; the deviations produced were read by means of the reflection from a mirror, which magnified them more than 200 times. The process for determining the rigidity was also described and illustrated by a figure; and the experiments in crushing were made upon columns of stone by means of a Bramah press. In experiments on the

rupture of the columns there was no marked deviation from the proportionality of strain to stress up to the breaking-point, except in the case of the marble. In crushing, the authors obtained considerably lower moduli than those quoted in tables for similar rocks; and as their experiments were performed upon columns about three times as long as their diameter, they repeated them upon columns of marble varying in length from one half to six times the thickness. The results seemed to show that the short specimens were the weakest; but there was little difference. The authors give the formulæ by which they worked out the results of each series of experiments, and bring together the mean results in a tabular form.

3. "The Glacial Deposits of West Cumberland." By J. D. Kendall, Esq., C.E., F.G.S.

The author gave a brief sketch of the physical geography of the district and of the distribution of the more remarkable and easily recognized varieties of rock. The glacial deposits, viz. Boulder-clays, sands, and gravels, occupy mainly the area of low ground skirting the hills, extending upward to a height of about 500 feet above the sea; above that contour-line they only occur in isolated patches or tongue-like prolongations up valleys to elevations occasionally of about 1000 feet. The deposits, where fully developed, consist of Upper Boulder-clay, Middle Sand and Gravel, and Lower Boulder-clay; together they sometimes attain a thickness of from 100 to about 130 feet. Certain peculiarities in the distribution of the deposits were described. The tripartite arrangement never occurs in the valleys in the mountainous district. Boulder-clays, indeed, sometimes occur here; but sands are more common. The distribution of the boulders from the more remarkable rocks was described; tables of these were given, as also of the maximum height above the sea at which each occurs. The origin of the deposits was next discussed. The author is of opinion that the presence in the Lower Boulder-clay of boulders derived from such widely different sources can only be explained by floating ice, but that the correspondence of the materials of the clay with rocks in the vicinity shows that glacier-mud produced the finer elements. The Middle Sand and Gravel he considers due to denudation of the above materials during a period of emergence. The Upper Boulder-clay he attributes to a second period of submergence corresponding generally in its conditions with the former one. The gravel mounds are probably caused by the stranding of bergs at the end of this period.

November 16.—R. Etheridge, Esq., F.R.S., President, in the Chair.

The following communications were read:—

1. Additional Evidence on the Land Plants from the Pen-y-glog Slate-quarry, near Corwen." By Henry Hicks, Esq., M.D., F.G.S.

2. "Notes on *Prototaxites* and *Pachytheca* from the Denbighshire Grits of Corwen, North Wales." By Principal Dawson, LL.D., F.R.S., F.G.S.

IX. *Intelligence and Miscellaneous Articles.*

ON THE DETERMINATION OF THE ILLUMINATING-POWER OF THE SIMPLE RADIATIONS. BY MM. A. CROVA AND LAGARDE.

ONE of the most delicate problems of photometry is the measurement of the illuminating-power of lights of different tints. One of us has already indicated\* how this question might be solved, by employing a spectrophotometer. That solution supposes that the coefficients of illumination of the different simple radiations composing the light which is to be compared are known.

If the determination of the radiant energy of a vibration of a determined wave-length can be expressed exactly in thermal or mechanical units, that of its illuminating-power admits of all the uncertainties inherent to the measurement of physiological sensations variable with each eye. There exists no known relation between these two quantities; we have therefore to commence by seeking out what are, for a determined eye, the illuminating-powers of the various simple radiations of the normal spectrum of two sources of light—the sun, and the Carcel standard.

The best-known treatise on this subject is that of Fraunhofer† on the Sun; the results obtained by him are not very concordant. The following is, briefly, the method which we have followed.

The illuminating-power of a simple light may be regarded as the property possessed by the latter of rendering distinguishable, upon a white screen illumined by it, minute details (lines, characters); it will be possible to measure them approximately, as several physicists have done, by weakening this light until the characters can no longer be distinguished, and taking the ratio of the initial intensity to this limit of intensity. The absolute value of these numbers will vary with the fineness of the characters; but their ratio will be sensibly constant, and will depend only on the wave-length of the light examined.

The light to be studied (sun or Carcel standard) is received perpendicularly upon the slit of a spectrophotometer covered with a strip of glass on which is photographed a series of very fine and very close dividing-lines; the direction of these lines cuts the slit normally. A pure spectrum is then seen furrowed by a considerable number of very fine longitudinal striæ. If the ocular slit of the telescope be brought onto a region of the spectrum, the simple radiations comprised between two very close known limits are isolated; and by a suitable rotation of the nicol, their intensity is weakened until the striæ cease to be perceptible. The phenomenon of the disappearance of the striæ is more delicate than one would have at first been inclined to believe; by practice one arrives at being certain about the degree or the fraction‡ of a degree, according to the region of the spectrum.

1. We have traced the curve of the wave-lengths as functions of the divisions of the micrometer, and calculated its equation by

\* *Comptes Rendus*, t. xciii. p. 512; *Phil. Mag.* Dec. 1881, xii. p. 445.

† *Gilbert's Annalen*, xxvi. p. 297 (1817).



the method of least squares. The derivate of that equation gives, for each wave-length, the factor by which the intensities of the prismatic spectrum must be multiplied to reduce them to those of the normal spectrum.

2. We have measured for wave-lengths comprised between 480 and 740, at intervals of 20 units, the rotations which cause the vanishing of the striæ.

3. The variations of the Carcel standard are corrected so as to reduce the intensity to the constant value corresponding to the consumption of 42 grams per hour; for this we made use of M. Deleuil's automatic balance, which registers, during the time of the experiments, the successive times required for burning 10 grams of oil. The solar light was diffused by a wooden screen whitened with carbonate of magnesia. We operated when the sky was very clear, about noon.

4. The prismatic curves have been reduced, as we have said, to the normal spectrum; and, lastly, the absolute maximum being set off upon the curve, we have reduced the ordinates to those corresponding to a maximum equal to 100.

The curves obtained are tangents at their two extremities to the axis of the wave-lengths; they rise at first slowly, afterwards very quickly in the vicinity of the maximum. For the lamp, the curve is nearly symmetrical on both sides of the maximum. For the sun, the ascent and descent are more rapid than for the lamp; the descent towards the violet is more rapid than the ascent on the red side.

The following results are deduced from the two most regular series, selected from amongst numerous determinations:—

Wave-length.....	740	720	700	680	660	640	620	600
Illuminating- { Lamp	0.1	0.7	1.6	5.7	14	28	52.5	94
powers ... { Sun...	...	...	...	0.5	1.5	4	10.2	23
Wave-length.....	580	560	540	520	500	480		
Illuminating- { Lamp	72.5	37.5	23.5	13.0	6.0	1.0		
powers ... { Sun...	62.5	98.5	30.5	17.2	9.2	3.5		

The maximum, =100, corresponds, for the lamp, to the radiation 592, and for the sun to 564.

The discussion of these results leads to conclusions which are in accordance with the theory of the emission of the radiations emitted by incandescent bodies\*.

The numbers obtained require a slight correction, on account of the absorption exerted towards the violet by the material of the prisms. We purpose to continue these determinations with prisms exerting no appreciable absorption upon the visible radiations.—*Comptes Rendus de l'Académie des Sciences*, Dec. 5, 1881, t. xciii. pp. 959-961.

\* *Journal de Physique*, viii. p. 357.

## THE PHOTODYNAMIC PARABOLOID.

BY PLINY EARLE CHASE, LL.D.

In the Philosophical Magazine for September 1876 I referred to evidences of parabolic influence between  $\alpha$  Centauri and Sun. The entire series of paraboloidal abscissas may be found in the Proceedings of the American Philosophical Society for June 17, 1881\*.

Newcomb gives estimates of the parallax of  $\alpha$  Centauri, which range between  $0''.48$  and  $1''.96$ . The mean of Henderson's observations in 1832-33, as deduced by himself, was  $1''.16 \pm .11$ . Peters, from the same observations, found  $1''.14 \pm .11$ . Henderson obtained  $0''.913$  from Maclear's observations in 1839-40; Peters,  $0''.967 \pm .064$  from the same; Maclear,  $0''.919 \pm .034$  from declinations in 1842, 1844, and 1848; Moesta,  $0''.880 \pm .068$  from declinations in 1860-64. There is therefore an uncertainty as to the actual distance, of the same order of magnitude as planetary eccentricities. If this fact should be thought to diminish the probability of a kinetic bond between the photodynamic paraboloid and the fixed stars, it will be well to bear in mind the following considerations:—

1. If there is an all-pervading interstellar medium, which is both material and elastic, all its persistent oscillations *must be* cyclically harmonic in some shape or other.

2. All such permanent rhythmical oscillations must be dependent upon or associated with permanent masses and velocities.

3. The mass and velocity from which the paraboloidal abscissas were deduced are Sun's mass and the velocity of light.

4. The coordinates indicate a solar motion in space which accords closely with Herschel's estimated velocity †.

5. The abscissas touch regions of incipient subsidence, which explain the formation of the several planetary belts, in accordance with Herschel's interpretation of the nebular hypothesis.

6. The abscissas are manifoldly grouped in ways that are phyllotactically and otherwise harmonically symmetrical, as might be looked for in a medium like the supposed luminiferous æther.

7. The last phyllotactic abscissa,  $A_{38}$ , is a fourth proportional to Sun's semidiameter, Laplace's limit of synchronous solar rotation and revolution, and the modulus of light at Sun's surface.

8. The paraboloid fixes Sun's position relatively to some other important stars in the Milky Way.

9. These are the most far-reaching indications of an unbroken chain of kinetic influences that have ever been published.

10. Being based upon the greatest mass and the greatest intercosmical velocity of which we have any measurable knowledge, the law of parsimony gives an *à priori* presumption that the chain may extend to other masses of a like order of magnitude with Sun.

11. The next abscissa to the solar phyllotactic series,  $A_{38}$ , is in

\* Vol. xix. pp. 447, 448.

† Proc. Amer. Phil. Soc., Nov. 4, 1881.

the region of the fixed stars, its locus being (within the limits of probable error) the same as that of  $\alpha$  Centauri.

12. The accordance of the terminal locus with that of  $\alpha$  Centauri *may be exact*; it is almost impossible that the deviation from precise accordance can be so great as 8 per cent.; and such a deviation could be easily explained by stellar orbital motions.

13. The second stellar abscissa,  $A_{40}$ , indicates a distance corresponding to Bessel's estimate of the parallax of 61 Cygni.

14. Whatever may be thought of the last three indications, the first ten are clear, unmistakable, and incontrovertible.

Haverford College, Nov. 15, 1881.

#### ON THE ACTION OF COLD UPON THE GALVANIC ARC.

BY D. TOMMASI.

When the galvanic arc springs between two metallic rheophores, of copper for instance, formed each of a tube bent in the shape of a U, through which a rapid stream of cold water flows, and placed horizontally one opposite to the other, the following facts are observed:—

(1) The illuminating-power of the arc is considerably weakened; it is reduced, so to say, to a mere luminous point, even when a very intense electric current is employed (50–75 Bunsen elements, large size).

(2) The arc, if it can be called so, is very unstable; the slightest breath suffices to extinguish it\*.

(3) If a sheet of paper be placed over the arc, at a distance of 4 or 5 millim., after a few moments a black point is seen to be produced, which extends and is at last perforated; but the paper does not take fire.

(4) The arc is constituted by a luminous globule moving up and down between the two rheophores. The form of this globule, as well as its extreme mobility, causes it to resemble very much a drop of liquid in the spheroidal state.

(5) If the south pole of a magnetized bar be brought near to the galvanic arc, the arc is attracted and approaches the magnet so that at length it leaves the rheophores and is extinguished. The same phenomenon is observed, but in a contrary direction, on bringing the north pole of a magnet towards the arc.

(6) The amount of ozone seems to be greater than when the arc is not cooled.

It is to be remarked that, in spite of the cooling of the rheophores, the flame of the arc is slightly green, proving that a portion of the copper burns. Hence one is entitled to ask if the arc would be produced by taking as rheophores two platinum tubes in which alcohol cooled to 30° C., for example, was caused to circulate.—*Comptes Rendus de l'Académie des Sciences*, Nov. 7, 1881, t. xciii. p. 716.

\* The instability is such that it cannot ignite a match without being extinguished itself.

ON THE VARIATIONS OF THE RESISTANCE OF ELECTRICAL  
MACHINES WITH THEIR VELOCITY. BY M. E. LACOINE.

It is known that the resistance of magneto- and dynamoelectrical machines is not constant, but increases with their velocity. The experiments of which I am about to give an account to the Academy afford ground for thinking that these variations of the resistance are to be explained by those of the contact between the movable commutator and the rubber-springs.

I employed a copper cylinder 5 centim. in diameter, with longitudinal grooves resembling the insulating ones of a Gramme's commutator. Upon this cylinder, at two diametrically opposite points, rub two steel springs which form the terminations of the two extremities of a circuit comprising a battery, a telephone, and a galvanometer to measure the resistances. The resistance of the circuit was :—

	ohms.
At rest . . . . .	68
With the velocity of 2000 rotations . . .	183
"      "      4000      "      . . .	900
"      "      about 5000      "      . . .	1567
With a very high velocity not measured	2900

The sound given by the telephone was the louder and shriller the greater the velocity.

In this first series of experiments every spring touched the cylinder over a space of three grooves; on making them touch over a greater extent (eight grooves), less sensible variations are obtained.

For each velocity the resistance diminishes when the pressure of the spring is increased. It is possible even to reach a pressure sufficient to suppress all microphonic effect and stop all sound in the telephone.

I have since modified the apparatus, and substituted for the fluted cylinder one of the same diameter but with its surface smooth. I obtained the same effects with a very little higher velocity. Instead of making the springs touch on the cylindrical portion, I caused them to press upon the plane lateral portion; the same results were observed.

The measurements which I have taken give me reason to believe that, for one and the same pressure of the springs, the increase of the resistance is proportional to the cube of the velocity; but it would be necessary to repeat these experiments with means which were wanting to me at Constantinople, in order to be assured of a constant velocity and to measure it exactly.

I will conclude by saying that with the telephone a more intense sound is heard when the intensity of the current is less; hence I conclude that the sound given by a telephone placed in the circuit of a Gramme machine is not due merely to the undulatory variations of the current, but also to the microphonic effect of the commutator.—*Comptes Rendus de l'Académie des Sciences*, December 5, 1881, t. xciii. pp. 958, 959.

THE  
LONDON, EDINBURGH, AND DUBLIN  
PHILOSOPHICAL MAGAZINE  
AND  
JOURNAL OF SCIENCE.

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[FIFTH SERIES.]

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FEBRUARY 1882.

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X. *On Integrating and other Apparatus for the Measurement of Mechanical and Electrical Forces.* By C. VERNON BOYS, A.R.S.M., Demonstrator of Physics in the Normal School of Science, South Kensington\*.

[Plates III., IV.]

WHEN in February of this year I described my first integrating-machine† before the Physical Society, I felt that, unless the tangent principle could be so applied as to admit of an indefinite growth of the integral, such principle would be useless for practical purposes. In that machine the integral is determined by the *position* of a cart, and so is limited by the size of the apparatus. Since that time I have devised a variety of methods of applying the tangent principle in which the integral is determined by rotation, and so there is no limit to the extent to which the integral may grow. In the following paper, which is divided into two parts, I have given in the first a description of a variety of integrating-machines, while in the second are some useful applications of the most simple form of integrator described in Part I.

PART I.

At the present time there seem to be three types of integrating-machines: 1st, those that may be called radius

\* Communicated by the Physical Society, having been read at the Meeting on November 26, 1881.

† Phil. Mag. May 1881.



machines, comprising Sang's planimeter, Clerk Maxwell's sphere machine, and Sir James Thomson's disk sphere and cylinder integrator (Ashton and Storey's steam-power meter also comes under this head); 2nd, sine or cosine machines, comprising Amsler's planimeter and mechanical integrator, and the various wind integrators; 3rd, tangent machines, which, so far as I am aware, are represented only by the cart machine already referred to and those that are the subject of this paper. This class of machines depends on the formula for integration, which, in its geometrical application, finds a curve of which the steepness or the tangent of the inclination (i. e.  $\frac{dy}{dx}$ ) is

equal to the ordinate of the given curve or to the given function. In my former machine a pointer is made to follow a curve, and by so doing causes a rod to be inclined in such a manner that its tangent is equal to the ordinate. There is also a three-wheeled cart; and the plane of its steering-wheel is by simple mechanism kept parallel to this rod; moreover the horizontal component of the cart's motion is equal to that of the pointer. Under these conditions the vertical component of the motion of the cart (or, shortly, its ascent) determines the integral.

I will now show how this principle is applied in a series of machines in which the integral is determined by rotation and not by linear motion, and in which, therefore, the integral may grow indefinitely. At first let us suppose that the cart in my first machine is incapable of vertical motion; then it, in its attempt to move up or down, will push the paper in the opposite direction. If now the paper is wound on a cylinder with its axis beneath the path described by the front wheel of the cart, and if the hind wheels are supported by some other means, then the cylinder will rotate; and the rate of its rotation will be proportional to the ordinate of the given curve, and the amount of its rotation will be the integral required. Now it will at once appear that the cart and the parallel motion are not wanted, and that the inclination of what was the front wheel of the cart, and what may now be called the tangent-wheel, may be determined mechanically by the same method that was adopted to give inclination to the rod. Also if, instead of moving the tangent-wheel along the surface of the cylinder, the cylinder be moved longitudinally under the tangent-wheel while its inclination is determined by suitable means, then, as before, the rotation of the cylinder is a measure of the integral.

As the cylinder must necessarily have a finite length, it cannot be caused to move continuously in one direction under

the tangent-wheel, but must be made to reciprocate. This motion is most readily produced by use of a "mangle-motion," which converts uniform circular into uniform reciprocating motion. Now, when the motion of the cylinder is reversed, so also is the direction of its rotation; and therefore either the action of the tangent-wheel on the cylinder must be reversed, or there must be a reversing-gear between the cylinder and the mechanism employed to count its revolutions. The action of the tangent-wheel on the cylinder is most easily reversed by having two of them mounted in a frame so that they lie in the same plane, but that one is on one side of the cylinder and the other is on the opposite side. The cylinder is made to bear against one during its forward stroke, and against the other during its return stroke—a change readily effected by the mangle-motion. Then the rotation of the cylinder is independent of the direction of its longitudinal motion. When it is preferred to use only one tangent-wheel, the reversal between the cylinder and the counting mechanism can be easily and perfectly produced by using three bevel wheels and a friction-clutch actuated by the mangle-motion or even by the change of motion of the cylinder.

If the cylinder could be made long enough and the ends bent round so as to join one another, then continuous revolution of the whole ring would take the place of the reciprocation of the cylinder, and the integral would be determined by the rotation of the ring round its circular axis. Such a "smoke-ring" can scarcely be made; but an equivalent can be produced without difficulty. Let there be four barrels, each with a concave instead of a convex outline, mounted on a wheel with their axes in one plane, and with some one generating line on each a quadrant of a common circle concentric with the axis of the wheel. Also let the four barrels be geared to one another by bevel wheels (fig. 1, Plate III.). Now let a tangent-wheel be placed inside the common circle so as to touch it at its lowest point; then, if the tangent-wheel lies in the same plane as the circle, revolution of the wheel supporting the barrels will produce no rotation of those barrels; but if the tangent-wheel is inclined at all, the rotation of the barrels will be directly proportional to the tangent of its inclination, and inversely proportional to the radius of the barrel at the point of contact. This periodical inequality, due to the changing radius of the barrel, may be eliminated by using a second mechanical smoke-ring made of a series of convex barrels mounted on a wheel, with some one generating line of each a portion of a common circle which lies outside instead of inside the barrels. In this, which may be called an outside

ring, the other being an inside ring, the barrels must not be geared together. Fig. 2 is a plan on a larger scale, partly in section, showing how such barrels might be supported. Now, if this outside ring is placed horizontally within the inside ring and touching it at one point, then revolution without rotation of the inside ring will cause rotation without revolution of the outside ring; if, however, in consequence of the inclination of the tangent-wheel, the barrels of the inside ring are caused to rotate, then such rotation will cause revolution of the outside ring; and this revolution will be a true measure of the integral, as the outside ring and the tangent wheel touch barrels of the inside ring at points having the same radius. The astronomical convention with respect to the terms revolution and rotation has been used. By revolution of the ring is meant a turning of the whole round a centre; and by rotation a turning of barrels round their own axes.

Instead of a disk, a sphere similarly mounted may be used for a tangent-wheel, with the same result. Of course the cylinder will be in contact with the sphere at a point on its equator; but if the support of this globe is varied in position, so that the cylinder touches the sphere nearer the poles, then the rate of rotation will depend not only on any former inclination of the plane of the equator of the globe to the axis of the cylinder, but will also be inversely proportional to the cosine of the latitude of the point of contact. The latitude should be brought back to its original value before the rotation of the cylinder is measured. Fig. 3 shows the cylinder in contact with the sphere at a latitude  $\lambda$ . It so happens that the radius in the sphere at the point of contact is equal to  $\cos \lambda \times$  the radius of the sphere; but this is not the cause of the introduction of that function, as the rotation of the cylinder is independent of the radius of the tangent-wheel. The true reason can be readily discovered by a simple geometrical construction, which, from the length of this paper, I omit. However, a good illustration may be seen by taking a bicycle and causing it to lean over on its side; then a given twist of the handles will be found to produce a greater deviation in the direction of its motion than would be the case if the bicycle were upright. The effect just described is most easily produced by mounting the cylinder on a rocking-frame, so that it can roll round the ball. Though the axis marked A in the figure remains vertical, yet the effect may be considered as due to a leaning to one side of this axis. If, however, the axis A is caused to lean forwards or backwards, then the rotation of the cylinder, which is still proportional to the tangent of any rotation about A, is also proportional to the sine of the

inclination of A above the horizon ; so that if A is horizontal, no rotation about A as an axis will produce any effect ; but as A rises higher, increased rotation of the cylinder will be produced, the maximum being when A is vertical. As in the former case, so here, the inclination of A should be brought back to its original value before the rotation of the cylinder is measured. This is the method of steering a wheelbarrow when pushing it. The elevation of the handles corresponds to the inclination of A with the horizon ; the equality of the elevation of the two handles corresponds to absence of rotation about A ; therefore the barrow goes straight. When turning a corner the outer handle is elevated more than the inner one ; this corresponds to rotation about A ; and the tangent of this rotation, multiplied by the sine of the elevation of the handles, measures the deviation of the barrow from its straight course. This deviation, then, is greater as the elevation of the handles is greater, and therefore in going round a sharp corner the handles should be raised as much as possible. By the means above described, either the quotient or the product of two functions may be directly integrated.

As in my former integrating-machine, so with these, the reciprocal of a function may be integrated by first inclining the tangent-wheel through a right angle ; then, when a function passes through 0 from + to -, the tangent-wheel describes on the surface of the cylinder a cusp showing a momentary infinite motion. A machine so arranged may be used to integrate, not the reciprocal, but the function itself, if, instead of moving the cylinder longitudinally, it is caused to rotate, when the longitudinal motion, or the number of reciprocations if suitable gearing is employed, will measure the integral. In a similar way the machine as first described will integrate a reciprocal.

If for any purpose, in addition to the total result, the integral up to any time is required, a diagram must be drawn. This can be effected by covering the cylinder with a layer of black tracing-paper, and allowing a band of paper as wide as the cylinder is long to pass between the tangent-wheel and the black surface. The length of paper passed through the machine represents the integral ; and the curve drawn shows its rate of growth continuously. Should it only be required to know the amount of growth during each of a series of short intervals of time, a narrow band (which is more manageable) may be used wrapped round a small wheel at the end of the cylinder, and so arranged that at the end of each double stroke of the cylinder it is caused to bear against the point of a stationary pencil ; then the pencil-marks represent equal intervals



of time, while the distances between them measure the average rate of growth over each interval.

I have at present supposed that the integrating surface is cylindrical; but other surfaces of revolution may be employed for particular purposes. As the rotation of the cylinder depends on the linear motion of its surface, it is clear that its rotation must be inversely proportional to its diameter. If, therefore, instead of a cylinder any other surface of revolution is taken, its rate of rotation will depend not only on the inclination of the tangent-wheel, but also on the radius of contact. The simplest case is that of a disk with the tangent-wheel mounted so as to be capable of radial movement. Then, if the tangent-wheel moves in the direction of its own plane, it will simply describe on the disk a radial line, and there will be no rotation; but if it is inclined at any given angle the disk will rotate, and the rate of its rotation will be proportional to  $\frac{1}{r}$ , and its whole rotation will be  $\int \frac{1}{r} dr$ , which is  $\log r$ . Now the tangent-wheel, in its movement outwards, describes on the surface of the disk a spiral which everywhere cuts the radii at the same angle; therefore in such a spiral the angles are the logarithms of the radii; *i. e.* it is the logarithmic spiral. If the inclination of the tangent-wheel is made to depend on some function, then such double-disk machine would integrate  $\frac{\phi x}{c+x} dx$ , in which  $c$  is the radius of contact when  $x=0$ .

If the axis of the tangent-wheel is made to pass through a fixed point over the disk removed from its line of travel by a right angle, then the tangent of its inclination to the direction of its motion is proportional to the radius of contact: but, other things being equal, the rotation of the disk is inversely as the radius of contact; therefore the amount of rotation of the disk for a given movement of the tangent-wheel is independent of the radius of contact, and the curve traced out on the disk is the spiral of Archimedes. But if, instead of passing over a disk, the tangent-wheel similarly mounted is made to pass along the surface of a cylinder, then the speed of rotation of the cylinder will be proportional to the distance of the disk from its neutral position, and its whole rotation will be  $\int cx dx$ , or  $\frac{c}{2} x^2$ , and the curve described on the cylinder will be a parabola. This arrangement of the disk and cylinder may be used, as described on page 84, in a polar planimeter to illustrate the formula  $\iint r dr d\theta$ .



After the cylinder and disk, the most simple form for an integrating surface is that of a sphere. Let a sphere be supported, with its axis horizontal, on a frame which can be made to reciprocate about a vertical axis which would, if continued, pass through the centre of the sphere; then, if a tangent-wheel is fixed so as to lie, when its inclination is nothing, in the horizontal plane which passes through the axis of the sphere, angular reciprocation, which must be less than  $180^\circ$ , will cause the tangent-wheel to describe on the sphere a meridian when it is in its neutral position, or a rhumb line if inclined at a constant angle. As the speed of rotation of the sphere is inversely proportional to the radius of contact—that is, to the cosine of the latitude of the point of contact—some means must be adopted whereby the rotation recorded is less than the rotation of the sphere in the same ratio. The most simple plan is to use Amsler's principle, and mount a small sliding and rolling wheel so as to be in contact with the sphere at the highest point on the equator (*i. e.*  $90^\circ$  from the tangent-wheel), but with its plane passing through the centre of the tangent-wheel; then the rotation of the Amsler wheel is always less than the rotation of the sphere, in the same ratio that the rotation of the sphere is too great. Instead of an Amsler wheel, a cylinder capable of moving longitudinally on its horizontal axis, and in contact with the sphere at a point exactly opposite to the tangent-wheel, would, by pure rolling and without any sliding, take off the correct proportion of motion, since it and the tangent-wheel always touch the sphere at points having the same radius.

Fig. 4 is a perspective view of a polar planimeter in which the integration is effected by a disk sphere and Amsler wheel, as described. All the parts marked *a* belong to a rigid frame, which balances on and can turn about a vertical spindle, the top of which is just visible below the tangent-wheel *t*. The vertical spindle is fastened to the stationary wheel *w*, which rests on three feet. The segmental wheel *W* in gear with *w* is secured to a vertical spindle, the upper end of which carries the crutch *C*. Screws in the crutch form the horizontal axis about which the sphere *S* may rotate. The tangent-wheel *t* is mounted in a frame which can be turned about a horizontal axis *e* by means of a lever *l*. The Amsler wheel rests by its weight on the highest point of the equator of the sphere, which is shown dotted. *DD* is an L-shaped piece, which carries at the angle the pointer *P*. At the end of the long limb is a slot embracing a pin, as shown. A part of the short limb is made cylindrical; against this part rests the edge of the lever *l*. This edge is not truly radial, but is

laterally displaced from the radial position to an extent equal to the radius of the cylindrical part of D D. This causes the true radius, which is parallel to the axis of the tangent-wheel, to intersect the axis of the cylinder. Now, if the pointer P is moved radially in the slot prepared for it, it is clear that the tangent of the inclination of the tangent-wheel  $t$  will be proportional to the square of the distance of P from the vertical axis about which the machine can turn, also that, during any turning of the machine about this axis, the sphere will turn about its vertical axis at a proportionate speed. Now it has been shown that, when the sphere is made to turn about its vertical axis, the rate of rotation of the Amsler wheel is proportional to such rotation multiplied by the tangent of the inclination of the tangent-wheel—that is, in this case to  $r^2 d\theta$ . Therefore the whole rotation of the Amsler wheel is a measure of  $\int r^2 d\theta$ ; and so, if the pointer P is taken round any closed curve, the area of that curve may be read off from the Amsler wheel. The wheel W is three times the radius of  $w$ ; so that the pointer may, if necessary, be taken completely round the pole, and yet the tangent-wheel will only move  $120^\circ$  on the sphere in latitude. The diameter of the Amsler wheel is one third of that of the sphere, so as to restore the diminished speed. Unlike Amsler's planimeter, this one shows the increment of area for each part of a closed curve, the reason being that it is an exact mechanical equivalent of the polar formula for integration. Though the machine works very well, it cannot be compared to Amsler's as a practically convenient instrument.

An exact mechanical equivalent of the formula  $\iint r dr d\theta$  would be produced by retaining all the last machine, except the short limb of the L-shaped piece D D, and mounting on the long limb a tangent-wheel to traverse a cylinder, the rate of rotation of which for a given radial movement of the pointer would be proportional to the distance of the pointer from the pole—that is, to  $r dr$ —and the whole rotation would be  $\int r dr$ . Now, if the cylinder were by its rotation caused to change the inclination of the lever  $l$  so that the tangent of the inclination of  $l$  was proportional to the whole rotation of the cylinder, then, when the pointer was taken round a curve, the rotation of the Amsler wheel would be  $\iint r dr d\theta$ . In either case, instead of an Amsler wheel, a cylinder mounted as described on the last page would give the integral.

## PART II.

The practical value of the tangent principle depends on the fact, that the only operation required of the function to be integrated is that of turning more or less a spindle and tangent-wheel, which may be as light and delicate as any part of a watch, and of which the moment of inertia may be inappreciable. This is in marked contrast to what is necessary in radius machines: the friction in the common double disk or disk and cone integrator, or the inertia of the ball in Sir James Thomson's machine, would be quite sufficient to make the former useless for the integration of such delicate forces as depend on the actions of electricity, or the latter inapplicable to machinery in rapid movement. Another point about tangent machines is, that the whole process of integration is the result of pure rolling, and any doubt that may be felt as to the effect of the sliding action on the accuracy of cosine machines is here removed. The rest of this paper describes some applications of the disk-cylinder integrator some of which are likely to be of practical value.

*Engine-power Meter.*

As work is motion multiplied by pressure, the work done in an engine may be found by integrating the difference of pressure on the two sides of the piston with respect to the motion of the piston. For any one stroke, this is usually done by measuring the areas of the indicator-diagrams, one taken at each end of the cylinder, and repeating, so as to get an average value. But as the work done, or the area of the diagram, is subject to variation depending on the load, pressure, and speed, only guesses can be made as to the whole amount of work that has been done by an engine during any length of time. Any machine, therefore, that will automatically find the total work done should be of value, not only to users of engine-power, but especially to experimentalists who are engaged on testing the efficiency of engines, and on other subjects where total work done should be known. It is only fair to mention that Messrs. Ashton and Story have an engine-power meter in which the integration is effected by a double-disk integrator acting on the radius principle; but it necessarily suffers from the defects common to all radius machines. The disk-and-cylinder is especially applicable to this particular case; for it is only necessary to make the cylinder reciprocate with the piston of the engine, the motion being of course reduced to a convenient amount, and to make the tangent of the inclination of the disk vary with the difference in pressure on

the two sides of the piston of the engine. Then, at any moment, the cylinder will turn with a speed which is proportional to the rate at which work is being done, and the number of revolutions, as measured by a counter, will be a measure of the work done in foot-pounds or other units during any time. Figs. 5 and 6 are views of an engine-power meter, each partly in section. A, A are two boxes with flexible covers, like the corrugated plate in an aneroid barometer. They may be filled with a mixture of glycerine and water or other liquid, and connected each with one end of the cylinder of the engine. Each diaphragm will feel the pressure, but not the heat, of the steam or gas in the cylinder. The two diaphragms are connected by the rod  $r$ ; and so the effective force tending to bend the diaphragms is the difference of pressure at the two ends of the cylinder. This is the force acting on the piston of the engine. Inclination is given to the tangent-wheel  $t$  by the rod  $r$  by a pin working in a radial slot, as is better shown in fig. 7. This arrangement causes the tangent of the inclination of the tangent-wheel to be proportional to the displacement of the rod  $r$ , and so to the force acting on the piston. C is the integrating-cylinder, which is capable of sliding along, but of turning with a wire W, which may be grooved or polygonal; pinion-wire is very suitable. The integrating-cylinder is caused to reciprocate, by means of a yoke Y and lever L, in time with the piston of the engine. The stroke is reduced to a convenient amount by attaching a string from the piston-rod to a suitable part of the lever L. Now, as the rate at which the cylinder turns is proportional to the longitudinal motion of the integrating-cylinder multiplied by the tangent of the inclination of the tangent-wheel, and as this is proportional to the motion of the piston multiplied by the force urging it, *i. e.* to the work being done, the whole number of the revolutions of the cylinder will measure the whole amount of work done. If the instrument gets out of adjustment so that the tangent-wheel is not parallel to the axis of the cylinder when there is no force, then whatever error it makes in a forward stroke it will take off in the return stroke; so that no accumulating error will be produced. The diaphragms may either be made of steel or highly elastic metal, in which case they form their own springs; or a softer metal, controlled by an external spring, might be used. If a diagram is required, one may be drawn as described on page 81. But it will not be a diagram such as is drawn by an ordinary indicator, but the integral curve of such a diagram; so that force, instead of being represented by the length of an ordinate, will be represented by steepness. Instead of diaphragms as described,

spring pistons or Bourdon pressure-gauge tubes might be employed to give inclination to the tangent-wheel.

### *Integrating Dynamometers.*

The disk-cylinder integrator may be applied to measure the whole amount of work transmitted by shafting or belting. In the case of shafting, what is called a differential coupling—that is, a contrivance which transmits any motion, but measures the force causing such motion—is employed to give inclination to the tangent-wheel. In the case of belting, any of the known dynamometers may be employed for the same purpose; while a mangle-motion driven by the revolving shaft or travelling band, causes the cylinder to reciprocate. Either of the methods given on page 79 may be employed to produce continuous growth of the integral in one direction. As the work transmitted at any moment is force multiplied by motion, and as the tangent of the inclination of the tangent-wheel is proportional to the force, while the reciprocating motion of the cylinder is proportional to the motion, the rate of revolution of the integrating cylinder will be proportional to the rate at which work is being done, and the whole number of revolutions will give the whole amount of work done. If at any time the force causing the motion should change sign and so resist it, as is the case in an engine when there is much cushioning, then the tangent-wheel will incline the other way and take off from the record a corresponding amount of work.

### *Electric-Current Meters.*

The application of the disk-cylinder integrator to an electric-current meter is very obvious. Figs. 8 and 9 are two views of an electric meter, in which the inclination of the magnet *M* is effected by the electric current passing in a large coil surrounding the instrument. The magnet *M* and the tangent-wheel *t* are each fixed on the same spindle, which is vertical, and which is very light and delicate. The weight of the magnet produces the necessary pressure between the tangent-wheel and the integrating-cylinder *C*; and as the surface of each is convex, the friction resisting the turning of the tangent-wheel by the magnet is very small. The cylinder is supported in a bell-crank frame *F*, which can be made to reciprocate along the wire *W* by means of the mangle-motion *m m*. The mangle-motion is actuated by clockwork, which may be wound by the current itself when necessary, should such a course be desirable. Fig. 10 shows the construction of a suitable mangle-motion. The pinion can turn, but not move otherwise,



while the frame carrying the racks can move either longitudinally or laterally. A pin projecting centrally from the pinion enters the slot, which is shaded in the figure, and so causes the pinion to gear with the two racks alternately. This lateral movement of the rack-frame is made use of to depress the integrating-cylinder during its back stroke, at which time the magnet rests on the shoulder S. As the tangent of the inclination of the tangent-wheel is proportional to the current-strength, and as the rate of rotation of the cylinder is proportional to the tangent of the inclination of the tangent-wheel, the cylinder will turn with a speed which is proportional to the current-strength, and the whole number of turns, as shown by the counter, will be a measure of the quantity of electricity that has passed. In the arrangement described, time is divided into a great number of equal intervals, and the current-strength during each alternate one considered. After any considerable time, such a sampling of the current would give just as exact a result as would be obtained by integrating continuously. A quick-return mangle-motion might be employed to diminish the proportion of ineffective time; or the whole time could be made effective by keeping the cylinder in continuous contact, and actuating a reversing-gear between the cylinder and a counter by means of the lateral movement of the mangle-motion. It would be well to employ a catch on the armature of a subsidiary electromagnet, so as to stop the clockwork, except when a current is passing. This current-meter, like Edison's electrolytic meter, is a direction-meter. If the current is passing in one direction, it counts it positive; if in the opposite direction, it counts it negative. A reverser actuated by a polarized armature could be employed to make the meter count as positive, a current passing either way, and so make it applicable to the case of alternating currents. Another kind of current-meter, which is by its nature independent of the direction of the current, would be preferable to the magnetic-needle meter and reverser combined.

Figs. 11 and 12 represent an electric-energy meter, which will be described later; but they will serve as diagrams to illustrate a description of the second current-meter. *mm* is the mangle-motion, which causes the cylinder *C* to reciprocate and bear alternately against the two tangent-wheels *tt*. These wheels are mounted in a common swivelling-frame, which ordinarily is kept vertical by the weights *XX*, but which may be inclined by a force due to any cause tending to turn the beam *B*. Now the turning-power of the weights *XX* varies as the sine of the inclination; while the turning-power of a force acting downwards applied to the point *p* varies

as the cosine of the inclination ; therefore the beam will set itself at such an angle that the tangent of the inclination is proportional to the force. If, therefore, the point  $p$  of the beam can be pulled downwards by a force which is proportional to the strength of the current, an electric meter will be the result. The coils shown in the diagrams, which belong to the energy-meter, must be removed and replaced by an electromagnet and armature of peculiar construction. Let there be an electromagnet with pole-pieces a certain distance apart, and let there be between them a wedge of iron at its narrow end increasing in thickness or width rapidly, and towards its thicker parts much more slowly ; then, on moving such a wedge forwards between the poles, but without touching them, it will at first facilitate by its movement magnetic induction at a great rate ; and as it fills up the space, even though the induction through it is greater, yet the increase of that induction is less. Now, as the rate at which magnetic induction is increased by movement measures the force with which such a wedge is pulled forwards, the wedge will, if suitably formed, experience a force with a given current-strength which is less as its entrance is greater, except over a small space near its starting position, where the force should, if possible, be infinite. Also, if the wedge is fixed in position and the current made to vary, it will, so long as the magnetic limit is not approached, experience a force which varies as the square of the current ; therefore, if the motion of the wedge is resisted externally by a force which varies as its displacement, it will enter to such an extent that the amount of its entrance is proportional to the current. Let such a wedge be carried by the beam  $B$ , so that when it is at its zero position the beam is horizontal ; then the inclination of the beam will be greater when the current is greater, and, except with very weak currents, may be made to vary so that its tangent is proportional to the current. The same principle might be applied in another way by causing rotation instead of linear movement of the armature to facilitate induction, and by resisting such motion by a pendulum-weight as before, or by a hair-spring. The armature then would have to be shaped something like an  $S$ , and adjusted experimentally so as to give, except with very small currents, a deflection whose tangent is proportional to the current. In Sprague's or Edison's electrolytic meters (the only ones of which I have heard which can lay any claim to being called current-meters at all) a portion only of the current is sent through the meter, and the rest passed by in a shunt. Now, if it were certain that the same proportion of the whole current always passed the meter, there would be

no objection to such a course ; but as a rise in temperature makes an electrolyte a better, and a metal a worse conductor, any electrolytic meter combined with a shunt would have a tendency to show too much in warm weather or if warmed by the current. If, again, there is any polarization, and that polarization is not strictly proportional to the current, then another error will be introduced. It would seem therefore necessary, if accurate indications are required, to make the whole current pass through an electrolytic meter.

### *Electric-Energy Meters.*

Since the energy expended by an electric current between any two points is equal to the current multiplied by the difference of potential of those points—that is, to the main current multiplied by a shunt current passing in a wire of high resistance between the two points—an electric-energy meter may be made by combining two electric-current meters, which take account of the direction in which the electricity passes, in such a way that the first integrates the main-current strength, and that the mangle-motion of the second is driven by the integrating-cylinder of the first : then, if the needle of the second is deflected by the shunt current, the rotation of the second cylinder will give the integral of the energy expended ; This is obvious ; for the rate of rotation of the second cylinder is proportional to its rate of reciprocation multiplied by the tangent of the inclination of its tangent-wheel—that is, to the strength of the current in the first machine multiplied by the strength of the current in the second ; so its rate of turning is proportional to the rate at which energy is being expended, and its whole rotation is a measure of the total energy. If at any time either the main or the derived current, but not both, changes sign, then the second cylinder will begin to turn the other way, showing that the current is not doing work in the portion of the conductor between the points, but is being caused to flow by an action of some kind taking place in that portion. If both currents change sign, then, as before, work is being done ; and though the first machine is working backwards, the second is working forwards. A combination of two machines, as described, would integrate both the current and the energy. A more simple and practicable machine for integrating energy alone is shown in figs. 11 and 12. The integrating mechanism has been already described ; the electrical principles employed must now be explained. If two wires, one conveying the main current and the other the derived current, are near one another, they will attract or repel one another with a force which is proportional to the product

of the two currents—that is, to the energy being expended; but if the wires are allowed to move, the force will depend also on the position. The question then is, how can the wires be so arranged that the force exerted may be used to incline the tangent-wheels and yet be independent of their motion. The arrangement of solenoids shown in section in fig. 12 is a complete and perfect answer.  $S_1$  and  $S_2$  are two fixed solenoids concentric with one another; and the main current is made to pass through each in the same direction.  $S_3$  is a solenoid made of a very great length of fine wire, preferably of aluminium silver, as suggested by Mr. Imray; and the upper half is wound in one direction and the lower half in the opposite direction; and the derived current is made to pass through it so as to pass in the upper half in the same direction as the main current passes in the fixed solenoids, and in the lower half in the opposite direction. This solenoid is hung in the annular space between the fixed ones by a band passing over the arc of the beam B. The tubes within and without the fixed solenoids and the rings above and below them, all of which are shown dark in the figure, are made of iron, and may or may not be used according as the currents employed are in general weak or strong. But whether the tubes are or are not retained, the use of the rings has certain advantages, which I now proceed to explain. Fig. 13 is a diagram taken by iron filings, which shows the distribution of the lines of force due to the fixed solenoids alone, without the tubes or rings. Here the lines of force cut the walls of the solenoid at an oblique angle, so that the force, which is at right angles both to the wires and the lines of force, tends to stretch the movable coil, and only a portion of it is effective in dragging down the solenoid: moreover the lines of force are very widely distributed over the solenoid, so that, unless it is of very great length, the upper part will leave by its motion many lines. It is true that on the lower end the movable solenoid will, when at its central position, enter as many lines in an element of motion as it leaves at its upper end; but after any considerable movement the upper end will leave many more than the lower end enters; and the force, as it is proportional to the number of lines enclosed, will become less as the solenoid moves from its central position. This will be referred to again later. Now the iron rings act as traps, so to speak, and catch nearly all the lines of force which without them stray over so great a space. Fig. 14 shows the field produced when the iron is present. It will be seen at once that nearly the whole of the induction takes place across a very narrow band of the solenoid, and that the lines of force,

where they cut the solenoid, are nearly horizontal; so that practically the whole of the force developed tends to drag the solenoid downwards, instead of being partly spent, as before, in producing a stretching strain. The consequence is that the movable solenoid may be made very much shorter than would be necessary if no rings were present. The tubes, having a higher coefficient of induction than air, merely serve to increase the number of lines of force, rather than affect their distribution.

If a movable solenoid, arranged as described, is hung by a band passing over the arc of the beam B, then the turning moment due to a down-pulling force is, within certain limits, constant, while the force restraining motion varies as the sine of the inclination of the beam; but had it been hung from the point  $p$ , the turning moment would have been proportional to the cosine of the inclination, and the tangent of the inclination would have measured the force. What is wanted is to make the tangent of the inclination proportional to the product of the two currents; and, as explained, this could be attained by using a long solenoid hung from the point  $p$ . But such an arrangement causes a double inconvenience; for not only is a long solenoid itself inconvenient, but the fact that it is hung from an arm and not from an arc causes a lateral shifting of the solenoid when the beam B is inclined, thus necessitating a wider annular space for it to pass through. Now the use of a comparatively short solenoid hanging from an arc introduces two errors which are almost absolutely equal and opposite. The error due to the arc is an increase of moment in the ratio of the cosine of the inclination of the beam to 1; that is, the error is equal to the versed sine of the inclination; and, like a thing that increases as the square of a quantity, it is at first quite inappreciable, and it increases in amount with increasing speed as the quantity grows. Now the error due to a short solenoid, such as shown in the figure, is at first nothing; for a given movement will cause the solenoid to enter as many lines of force at one end as it leaves at the other, but as it gets displaced it enters rather fewer than it leaves; and this difference in the number of lines of force increases in amount with increasing speed. Now, if the proportions are so taken that when the inclination of the beam is a little less than the greatest amount permitted to it the actual magnetic error is equal and opposite to the versed-sine error, then, since each is a quantity which grows according to the same kind of law, those errors will be always approximately equal, and their differences very small compared with the errors, and absolutely inappreciable in comparison with the



quantities of which the errors themselves are small. The geometrical representation (fig. 15) makes this clearer. The two sets of errors may be considered as ordinates of two curves drawn to the same abscissa. The point  $p$ , where the curves intersect, corresponds to that inclination at which the two errors are made equal, and the origin  $O$  to the central position. Since both errors are of a kind which are inappreciable at first, the two curves will have the axis of  $x$  as a tangent; and since the two errors are of a kind which grow in the same kind of way, *i. e.* at first slowly, and at an increasing rate as they grow, the curves must be nearly similar; and since they have the common point  $p$ , they must be nearly identical. The distance between the curves at any part gives the actual error there; and this being small in comparison with the ordinates at that part, is inappreciable in comparison with the whole distance of that part from the line  $zz$ . In the particular case the ordinate  $pm$  is about 4 per cent. of  $pQ$ ; so the actual error may be safely neglected. But, finally, should there be any error that can be detected at all, such error may be almost entirely eliminated by putting a few extra turns of wire near the ends or the middle of each half of the movable solenoid, according as the curve of the magnetic error between  $O$  and  $p$  is below or above the curve of the versed-sine error.

Assuming the truth of what is stated in the last paragraph, we find the tangent of the inclination proportional to the rate at which energy is being expended. But the speed of rotation of the cylinder is proportional to the tangent of the inclination; therefore the number of turns of the cylinder, given by the counting-mechanism in the box over the cylinder, is a measure of the total energy expended. As in the other energy-meter, so in this, if the electric current is helped at any time instead of being used, then the integrating-cylinder will turn the other way, and take off from the record an amount which is a measure of the work expended on the current.

There is a point about the solenoid energy-meter which is worthy of notice. The movable solenoid has an equal number of turns in opposite directions; so it is independent of the magnetic field in which the instrument is placed, and so this meter may be used in workshops or near dynamo-machines without its action being interfered with. For the same reason, when used in houses as gas-meters are for gas, it will be impossible for the householder to tamper with its indications by placing magnets round the instrument.

When very powerful currents are employed, it is well to shunt a certain proportion of the main current past the meter, or, when the electromotive force is very great, to introduce

into the secondary circuit resistance-coils. To prevent waste of clockwork energy or of electricity, the main current is made to pass round a subsidiary electromagnet whose armature allows the clockwork to go only when the main current is passing. This armature also, on being attracted, completes the secondary circuit, so that the derived current can only flow when the main current is passing.

The meter may be used as an energy measurer or indicator (not meter) with advantage when setting the carbons of an electric arc. If the two poles are made to touch, though the current is enormously increased, the energy is reduced, owing to a greater falling-off in the difference of potential between the poles. As the carbons are gradually separated the current diminishes, but the difference of potential increases in a higher ratio; so their product increases; that is, the energy expended, and so the heat and light produced, increases. This increase is shown by an increased inclination of the beam. After a time a point is reached at which the current decreases in the same ratio that the difference of potential increases; at this point the inclination of the beam attains a maximum; beyond this the decrease of the current is in a higher ratio than the increase in the difference of potential, so the energy, heat, and light fall off, as is indicated by the diminution of the inclination of the beam. If, therefore, the carbons are placed so that the inclination of the beam is a maximum, then the best effect is being obtained. In the same way, if the current is being employed to drive a machine, the most effective speed for that machine may be found by observing at what speed the inclination of the beam is greatest.

The various meters described depend for their numerical results on two things—(1) the horizontal intensity of the earth's magnetism, (2) the force of gravity. The indications of the first current-meter are inversely proportional to the horizontal intensity, and of the first energy-meter to the square of the horizontal intensity. Each of them is disturbed by changes in the direction of the earth's magnetism.

The second current-meter and the second energy-meter are independent of the magnetic field altogether. Their indications vary inversely as  $g$  when the clockwork is regulated by a balance-wheel, or inversely as  $\sqrt{g}$  when a pendulum-clock is used. This dependence on gravity is a point of very great importance; for over any one country gravity does not change appreciably, nor does it matter in what direction the machine is placed so long as it is level. By screwing the weights *XX* up or down, so as to decrease or increase the influence of gravity on the meter, its indications may be regulated to a

standard measure. Therefore, in making the coils, there is no necessity to count the number of turns exactly, or to lay them with the utmost accuracy: they may be wound in the ordinary way, and then a hundred machines or more connected together, with the main circuits in series and with the derived circuits in series, and a current sent from a suitable source through each series; then, if there is one meter which has been standardized by careful experiment, all the rest can be regulated, just as clocks are, by screwing down the weights X X of those that are going fast, or screwing up the weights of those that are going slow.

If in the foregoing paper any of the apparatus is not as fully described as it might be, I must plead as an excuse an endeavour to occupy a reasonable space with an account of what is essentially one invention.

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XI. *The Experimental Comparison of Coefficients of Induction.*  
By HERBERT BARFIELD, B.Sc.\*

OF all electrical investigations, the experimental comparison of coefficients of induction is one of the most difficult to carry out with accuracy; and it is doubtless most desirable that we should be able to compare such quantities much more accurately than has been hitherto possible. The usual methods, as far as their general arrangement is concerned, are in all probability not capable of improvement; but, as carried out, there is one modification applicable to all of them, by which the sensitiveness can be vastly increased. This modification is in the use made of the galvanometer. Hitherto it has been usual to observe the throw of the needle due to the passage of the quantity of electricity in one transient current; but if, instead of doing this, we pass through the galvanometer a number of such quantities in rapid succession and (after the manner of Siemens and others) observe the permanent deflection of the needle, we shall find this far greater than any throw attainable by even the most suitable apparatus.

In fact, the permanent deflection due to a certain number of transient currents per second may be compared with the throw of the needle due to one of them, in the following manner:—Let

H represent the magnetic force acting on the needle,

G the galvanometer-constant,

M the magnetic moment of the needle,

$\tau$  its time of vibration,

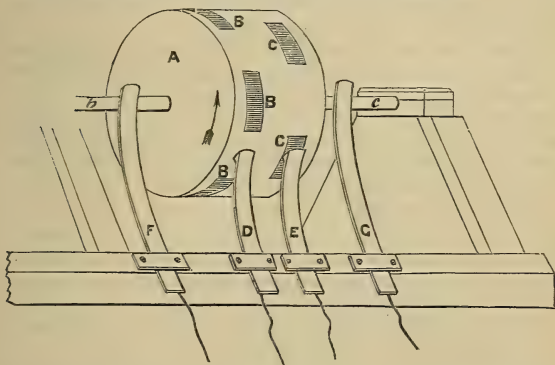
\* Communicated by the Author.



the apparatus would fix a limit far before any such speed was reached. It does not, however, appear to be beyond the mark to say, that the sensitiveness could be in this method made fifty times as large as that of the ordinary mode of experimenting.

The conclusion expressed in equation (3) has been *experimentally* verified by comparing  $\phi$  and  $\theta$  with the following arrangement:—A single Leclanché cell sends a current through the primary of a certain pair of coils. The secondary is connected up to the galvanometer; and the induced current at breaking is used to deflect the needle.

To obtain a constant succession of transient secondary currents in the same direction, the apparatus shown in the sketch is used:—A is a cylinder of hard dry wood  $5\frac{1}{2}$  inches in diameter, which rotates on its axis  $bc$  in the direction of the arrow. On the surface of A are fixed the brass strips B, C, five in each row: the pieces B are in metallic connexion with each other and also with  $b$ ; similarly the pieces C are con-



nected to the other end of the axis  $c$ . F, G are springs keeping an electrical contact with  $bc$  respectively whilst the axis rotates. D, E are springs pressing firmly on the cylinder, and making contact with the brass strips when they pass underneath. F, D are inserted in the primary circuit; E, G in the secondary. Thus the secondary circuit is only closed between each break and make of the primary; and only the induced current at break flows in it.

It is found that when the cylinder is rotated, a steady deflection of the needle is obtained, which increases with the speed of rotation, as equation (2) leads us to expect.



With the coils mentioned above and with one Lechanché in the primary,  $\theta$  was 13 scale-divisions (the galvanometer being shunted),  $\tau$  was  $7\frac{1}{2}$  seconds, or about  $2\pi$ . When the cylinder was making about 4 revolutions per second (giving 20 breaks per second),  $\phi$  was found to be a little over 500; that is, the light was off the scale.

Now equation (3) gives

$$\phi = 2n\theta = 520.$$

This shows that a value of  $\phi$  enormously in excess of  $\theta$  may be obtained; and though the experiment is only a rough proof of equation (3), it serves to show the greatly increased sensitiveness obtained.

Other experiments of a similar nature were made; but, being merely confirmatory of this, they need no further mention. It is possible that a powerful vibrator might with advantage be substituted for the rotating cylinder; and this would be completely self-acting; but it is doubtful whether it would be easier of manipulation than the cylinder, which can be very conveniently worked by a treadle, thus leaving the hands quite free to adjust the resistances.

In using the rotating cylinder with the bridge, E G would be inserted in the "bridge wire;" and since that is thereby broken whenever the battery is on, the effect due to the induced current is separated from that due to any very slight derangement of the balance—a great advantage when it is remembered how troublesome the presence of this latter effect is liable to be with the ordinary arrangement.

Derby, December 30, 1881.

## XII. *On Sound-Shadows in Water.* By JOHN LECONTE\*.

1. **M**ORE or less perfect sound-shadows thrown by hills, buildings, piers, and other obstacles to the transmission of aerial vibrations, must be within the experience of all. Nevertheless the boundaries of such shadows are so imperfectly defined, that they can hardly be compared, except in a general way, with those of light. Moreover, in some cases the obstacles placed in the route of the sound-waves, being elastic, propagate more or less perfectly the sonorous vibrations of the air through their thickness; so that, under these conditions, it is similar to producing a light-shadow by means of a transparent or translucent body.

2. But even in cases in which the sound-vibrations in air are not sensibly transmitted through the intervening obstacle

\* From advance sheets of the 'American Journal of Science,' vol. xxiii. January 1882. Communicated by the Author.

the boundaries of the sound-shadows are necessarily very imperfectly defined; for the amount of diffractive divergence proceeding from the secondary waves, originating at the boundaries of the obstacle and propagated within the geometrical shadow, is usually so considerable that the diminution of intensity of sound behind it, although quite perceptible, is by no means so conspicuous as might be expected.

3. The contrast, in this respect, between sound and light is well expressed by Lord Rayleigh:—"When waves of sound impinge upon an obstacle, a portion of the motion is thrown back as an echo, and under cover of the obstacle there is formed a sort of sound-shadow. In order, however, to produce shadows in any thing like optical perfection, the dimensions of the intervening body must be considerable. The standard of comparison proper to the subject is the wave-length of the vibration; it requires almost as extreme conditions to produce rays in the case of sound, as it requires in optics to avoid producing them"\* . In other words, the difference between sound and light results from the well-known fact, that an ordinary obstacle bears an immense ratio to the length of a wave of light; but does not bear a very great ratio to the length of a sound-wave. Hence it follows, from the mathematical theory of undulations, that the waves of sound bend around obstacles, and produce more or less effect within the geometrical shadow, whereas light-shadows have definite boundaries and are more sharply defined. For, in the case of light, calculation shows that at any point decidedly within the geometrical projection of the obstacle from the luminous source the disturbance vanishes, while at any point outside of the geometrical projection the disturbance is the same as if the primary wave had passed the screen unimpeded. But this is only partially true in the case of ordinary sound-waves, in consequence of their considerable length; it is rigorously true only when, as in optics, the diameter of the obstacle is large in comparison with the wave-length.

4. There are, however, other causes, depending upon the differences between the sense of hearing and of sight, which doubtless render the appreciation of the shadows of sound much less distinct than those of light. On this point, Lord Rayleigh justly remarks:—"In many cases sound-shadows appear much less perfect than theory would lead us to expect. The anomaly is due in a great measure, I believe, to an error of judgment, depending on the enormous range of intensity with which the ear is capable of dealing. The whistle of a

\* 'Theory of Sound,' vol. ii. p. 106, art. 283. London, 1873.

locomotive is very loud at a distance of ten yards. At a mile off the intensity must be 30,000 times less; but the sound still appears rather loud, and would probably be audible, under favourable circumstances, even when enfeebled in the ratio of a million to one. For this reason, it is not easy to obtain complete shadows"\* . In other terms, the range of audition is so extensive, that the diffractive secondary waves originating at the boundaries of the obstacle and propagated into the geometrical shadow, though comparatively feeble, produce decided sensuous impressions upon the auditory apparatus of the ear.

5. The mathematical theory of undulations indicates that acoustical shadows should be more distinct for short waves than for long waves. This prevision has been verified by the experiments of Lord Rayleigh†, who found that the sound-shadows cast by acute sounds were more distinct than those produced by grave sounds.

6. Another prevision of theory has been experimentally verified both in the case of light and of sound. It is well known that the great geometer Poisson, in applying Fresnel's integrals to the case of the diffraction of light produced by a small opaque circular disk, was led to the startling result that the illumination of the centre of the shadow was precisely the same as if the disk had been altogether removed. This deduction from theory was experimentally verified by the illustrious Arago, by means of an opaque circular disk 2 milim. in diameter; for he observed a bright point in the centre of the shadow of the disk on which waves of light were directly incident. In this case the secondary waves originating at the disk find the conditions of complete concurrence at a definite point in the axis of the geometrical shadow.

7. The difficulties to be overcome, in the experimental verification of the acoustical analogue of this beautiful phenomenon, are entirely different from those of optics, on account of the immense disproportion of wave-lengths. In light, the disk must be small, and the luminous source must have a very small angular magnitude. In sound, the disk must be comparatively large, and the sounds must be acute. Lord Rayleigh has recently succeeded in experimentally verifying this prevision of theory in the case of sound, by means of a circular disk about fifteen inches in diameter, with a bird-call as the source of sound, placed at a distance of twenty inches from the centre of the plane of the disk. At twenty-four

\* Phil. Mag. 5th series, vol. iii. p. 458 (1877).

† Ibid. pp. 458, 459 (1877).

inches on the further side of the disk, the augmentation of the intensity of the sound, in the axis of the acoustical shadow, was obvious both to the ear and to a sensitive flame\*.

### SOUND-SHADOWS IN WATER.

8. It is a significant fact in relation to the phenomenon of acoustical shadows, that they seem to be more perfect or more sharply defined in water than in air. Thus, during the progress of the classical experiments of Daniel Colladon, in November 1826, on the velocity of sound in the waters of the Lake of Geneva, this physicist incidentally observed that when the end of the hearing-tube (*cornet acoustique*), plunged into the water, was screened from rectilinear communication with the bell by a projecting wall running out from the shore, whose top was above the surface of the lake, there was a very remarkable diminution in the intensity of the sound, in comparison with that observed at a point equally distant from, but in direct communication with, the source of sound, or out of the "acoustic shadow," thus indicating the relative non-divergence of the rays of sound around obstacles in water as compared with those in air†.

9. Another fact observed by Colladon during these famous experiments is, in this connection, no less significant. He found that the sound of the bell struck under water, when heard at a distance, has no resemblance to its sound in the air. Instead of a prolonged tone, a short sharp sound is heard, like two knife-blades struck together. It was only within 200 metres that the musical tone of the bell was distinguishable after the blow. In air, it is well known, the contrary takes place—the shock of the first impulse of the hammer being heard only in the immediate neighbourhood of the bell, while the continued musical sound is the only one that affects the hearing at a distance‡. Sir John Herschel, in his Treatise on Sound §, promised to explain this curious difference, but has not, so far as I can find, done so. Colladon|| explains this phenomenon by the nature of the sonorous vibrations in water, showing that the duration of the sound will be much less when transmitted by water than when propagated by air.

### EXPERIMENTS OF L. J. LeCONTE IN 1874.

10. The preceding remarks show that comparatively few exact observations have been made on the obstruction pro-

\* Phil. Mag. 5th series, vol. ix. pp. 281, 282 (1880).

† *Ann. de Chim. et de Phys.* 2nd series, vol. xxxvi. pp. 256, 257 (1827).

‡ *Op. cit. supra*, p. 254.

§ *Encyc. Metrop.* art. 101.

|| *Op. cit.* p. 255.

duced by interposed obstacles to the propagation of sound-waves in different media. The following experimental results in relation to acoustical shadows in water may be of interest to physicists. The experiments were executed in 1874\*, at my suggestion, by my son, L. J. LeConte, during the engineering operations incident to the removal of "Rincon Rock," a sandstone reef in the harbour of San Francisco (near the south-eastern water front of the city), by means of "surface blasting" with "giant powder" or dynamite. The depth of water on the reef was about fifteen feet at low tide, with an extreme tidal range of about six feet. The "cans" or "cartridges" of "giant powder" used contained each about fifteen pounds of the explosive compound, comprising about 75 per cent of nitro-glycerine.

11. *Effects of the Explosive Shock.*—It was observed that the suddenness of the shock imparted to the water by this explosive agent produced the most remarkable and astonishing effects. At the distance of 300 feet or more from the detonating cartridge, two distinct shocks were experienced. The first shock came through the intervening water, and was felt as a short concussion or click before there was any sensible elevation of the column of water resting over the point of explosion. The second shock came a little later by the air, and was heard. It was evidently communicated to the air by the water, at the time the elastic pulse transmitted by this liquid (the first shock) emerged, in a direction nearly normal to its surface, over a limited area around a point vertically above the exploding cartridge. This was obvious from the fact that aerial sound came from this region. The area which was the source of the sound transmitted by the air, was the same as that from which the small jets of water (noticed hereafter, 14) were projected. The gases generated during the explosion came to the surface much later than this shock, and after elevating the column of water over the position of the cartridge to the height of twenty-five or thirty feet.

It is the character of the first shock that deserves special notice. To a person sitting in a small boat floating on the water at a distance of 300 feet or more from the point of explosion, with his feet resting on its bottom, the shock was felt as a sudden blow applied to the soles of the feet. In fact, it drove out the oakum from the seams in the bottom of the boat. When the observer stood on the top of a vertical wooden pile, this shock was felt as a sudden concussion coming up from the

\* The long delay in writing out the notes of these experiments in form for publication has been due to domestic affliction and the subsequent pressure of perplexing duties.

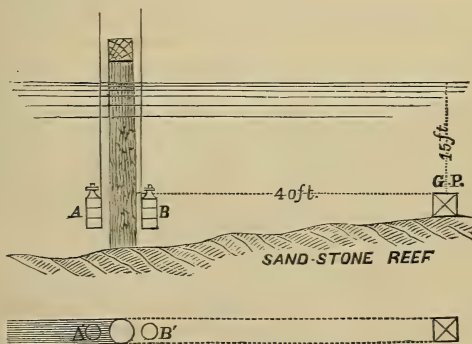


water along the cylinder of wood. The concussion produced by such an explosion was so violent that it killed or stunned the fish in the water within a radius of 200 or 300 feet from the explosive centre. They rose to the surface in a helpless condition, and were secured by the boys.

### EXPERIMENTS ON SOUND-SHADOWS.

12. *Experiments with stout glass (soda-water) Bottles.*—In these experiments the observer stood on the top of a vertical cylindrical pile (the trunk of an Oregon pine) about one foot in diameter, situated about forty feet horizontally from the explosive cartridge. The bottle, being secured to a rigid rod, was first plunged under the water from ten to twelve inches behind the pile (fig. 1, A), that is within its geometrical shadow. The shock of the explosion did not injure the bottle. It was then plunged into the water in front of the pile (fig. 1, B), or outside of its geometrical shadow. In this position the bottle was shattered to atoms by the concussion due to the explosion. As viewed from the experimenter's situation on the top of the pile, fig. 1, A' and B' indicate the two positions of the bottle in the preceding experiments.

Fig. 1.

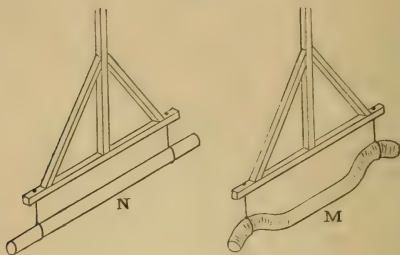


The experiments were varied by plunging bottles into the water in various positions around the pile, within and outside of its geometrical projection from the explosive centre; and in all cases they were protected from injury when within the geometrical shadow, and were shattered when outside of the same. The same results took place whether the bottles were filled with water or with air.

The breaking of a glass vessel by a sudden shock communicated by means of water is a fact long known, and is illustrated by the old familiar class experiment of exploding a "Prince-Rupert drop" while its bulb is plunged into an ordinary apothecary's phial filled with water.

13. *Experiments with stout glass Tubes.*—The cylindrical glass tubes employed were about 6 feet long and 1.5 inch

Fig. 2.



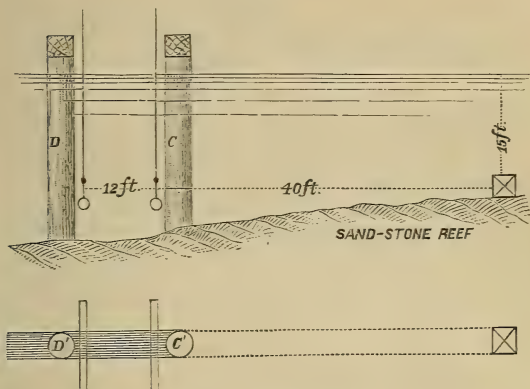
in diameter, the glass being about 0.5 of an inch in thickness. They were covered by pasting cartridge-paper over them, so as to prevent the loss of fragments when breakage occurred. (See fig. 2, M.)

The tubes were adjusted to a framework of wood so arranged (fig. 2, N) that they could be plunged in a horizontal position beneath the surface of the water behind the pile, the axis of the tube being at right angles to the plane of its shadow, and held there (the observer standing as before on the top) with the middle of the tube in the geometrical shadow, while the two extremities projected on either side about 2.5 feet beyond the boundaries of said shadow. (Fig. 3, C and C'.) In every case the shock of the explosion shivered the projecting portions of the tube, and left the portion within the shadow uninjured. The boundaries between the broken and the protected portions of the glass were sharply defined. ✕

By standing on the top of a second pile, in the direction of the axis of the shadow of the first pile, and distant about 12 feet, the experiments were varied by plunging the framework and tubes—adjusted at right angles to the plane of the prolonged shadow—into the water at this distance (12 feet) from the obstacle which obstructed the sound-wave transmitted by the liquid. (Fig. 3, D and D'.) The shock of the explosion produced sensibly the same results as when the tube was near to the obstructing obstacle. The protected portion of the horizontal glass tube was sensibly equal in length to the diameter

of the pile casting the shadow; hence the shadow of the cylindrical pile extended back for about 12 feet between sensibly parallel vertical planes, and its boundaries, at this distance, were still sharply defined.

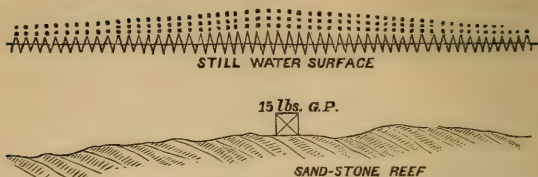
Fig. 3.



It is evident that, if the explosive centre were of insensible magnitude, the horizontal thickness of the geometrical shadow of the pile, at a distance of 12 feet beyond it, would be augmented in the ratio of 40 to  $40 + 12$ , or of 40 to 52, these numbers being the distances in feet from the centre; so that, if the thickness of the shadow at the pile were 12 inches, its thickness at 12 feet beyond would be 15.6 inches. If, however, the explosive energy occupied more or less space (as was the case in relation to the "giant-powder" cartridges), the thickness of the geometrical shadow or umbra cast by the pile might not increase sensibly with augmenting distance; and, indeed, in case the exploding body exceeded 12 inches in diameter the thickness of the shadow would diminish with increasing distance from the obstructing pile, as in the case of the umbra cast by an opaque body which is smaller than the luminous source.

14. *Another Phenomenon observed.*—Another interesting phenomenon came under our notice during the execution of these experiments. It was the singular effects observed on the surface of the water (when perfectly calm and glassy) for a certain area around the point immediately over the exploding cartridge. Simultaneous with the first shock (11) trans-

Fig. 4.



mitted by the water—and before the ascending gases of explosion disturbed it—the surface of the liquid exhibited numerous jets of water, rising to the height of about 3 inches over the centre of the area, and diminishing in height with augmenting distance from the centre. The appearance presented was not unlike that produced by a heavy shower of rain falling on the calm waters of a lake (fig. 4). To an observer in a boat floating on the adjacent water, and consequently viewing the phenomenon from a point near the water-level, there seemed to be a curious quincunx-like arrangement of the jets.

#### EXPLANATION OF THE PHENOMENA OBSERVED.

15. *Greater Distinctness of Sound-Shadows in Water.*—The much greater distinctness of acoustical shadows in water, as compared with those in air, appears to be pretty clearly established by the experiments of Colladon; and the fact seems to be abundantly confirmed by those which we have recorded in the preceding pages. This is an interesting and significant phenomenon in relation to the theory of sound. At first sight it might be supposed that the difference is due to the greater velocity of propagation of the sound-wave in water. This may have been Sir John Herschel's idea when he explained Colladon's results by reference to the greater elasticity of water\*.

But, as already indicated (3), according to the mathematical theory of undulations, the intensity of the effects due to the secondary waves propagated into the geometrical shadow from the borders of the obstacle is not directly dependent upon the velocity of propagation, but is properly a function of the wave-length, the diffractive divergence being less for short than for long waves. Hence it follows that the distinctness of sound-shadows, like those of light, should depend upon the shortness of the wave-length. We have already seen (5) that experiment verifies this prevision of theory in the case of sound-waves in air, by demonstrating that acute sounds cast more distinct shadows than grave

\* "Treatise on Sound," Encyc. Metrop., art. 102.

sounds. Does this principle apply to sound-shadows in water?

Some physicists have attempted to explain the phenomenon of the great distinctness of sound-shadows in water, as indicated by the observations of Colladon (8), by assuming that the lengths of the sonorous waves propagated through water are much shorter than those transmitted through air\*. But no reason is given for this fundamental assumption, other than that it is required by the demands of the theory of undulations, in order to account for the more perfect shadows in water. It evidently would be vastly more philosophical to establish as a matter of fact the greater shortness of the sound-waves in water, and thus to verify the deductions of theory. This we shall endeavour to accomplish.

16. *Measurement of Wave-lengths.*—With regard to continuous or musical sounds, we have the means of very readily determining the wave-length; for it is equal to

$$\frac{\text{Velocity of Sound}}{\text{Number of Vibrations}}$$
. It is evident, therefore, that, the number of vibrations or musical pitch of the sonorous body remaining the same, the wave-length in water, so far from being shorter, must be more than four times as long as they are in air. Hence, according to theory, if Colladon's observations had been within the radius (200 metres) at which the musical tone of the sonorous bell was heard, the sound-shadows would have been less distinct than in air. Unfortunately, Colladon does not inform us at what distance from the vibrating bell his observations in relation to the acoustical shadows were made; so that it is impossible to apply this critical test of the theory of shadows. But the presumption is, that the observations were made in the neighbourhood of Thonon (while the sonorous bell was placed at Rolle), at a distance of 13,487 metres from the source of sound, these being the arrangements during the execution of the experiments for determining the velocity of sound in the waters of the Lake of Geneva. At all distances from the bell greater than 200 metres, as we have seen (9), the sound lost its *musical* character and became short and sharp, like two knife-blades struck together. Hence, under the assumption that the observations on sound-shadows were made very far beyond the limits at which musical tones were transmitted, we are precluded from determining the wave-length by the number of vibrations. It appears that in water grave sounds are more rapidly suppressed or damped than acute sounds; so that at

\* Vide W. H. C. Bartlett's 'Elements of Natural Philosophy,' "Acoustics and Optics," 4th ed., N. Y. 1866, p. 75, art. 66.



moderate distances from the sonorous centre only the short and sharp sound due to the shock of the striking hammer was transmitted to distant points through the water. It is obvious that the wave-lengths of sounds of this character must be determined by other considerations than those relating to the musical pitch.

In relation to solitary waves generated by sudden blows and explosions\*, it may be more difficult to form a just estimate of the wave-length than in the case of musical sounds. Nevertheless it is evident that the wave-length must be directly proportional to the time occupied by the displacing impulse, multiplied by the velocity of transmission of the elastic pulse. In algebraic terms, if  $L$  = wave-length,  $t$  = time of the generating impulse, and  $v$  = velocity of sound in the elastic medium; we have,  $L$  varies as  $t \times v$ , or  $L = t \times v$ . Consequently, in a given medium, in which  $v$  remains constant,  $L$  will be a function of  $t$ , or the duration of the generative impulse; so that when the factor  $t$  is indefinitely small, the value of  $L$  will be

\* It may be questionable whether the elastic waves generated by momentary explosions or detonations can be properly regarded as strictly solitary. It is possible that, in such cases, groups of waves are generated similar to those discussed by Lord Rayleigh in the Appendix to his work on the Theory of Sound, vol. ii. pp. 297-302.

Furthermore, the admirable and exquisitely refined arrangements devised by Regnault for investigating the phenomena of sound enabled him to submit this question to a more or less satisfactory experimental test, so far as aerial waves are concerned (*Mémoires de l'Acad. des Sciences*, vol. xxxvii. pp. 45-49 et pp. 278-282; Paris, 1868). He found that the explosion of a pistol charged with ordinary powder does not produce only a single wave, since it gave rise to a recognizable musical tone of very brief duration (p. 45); and the same was the case with the sound produced by the detonation of a mixture of oxygen and hydrogen gases (p. 48). But the explosion of a small charge of fulminate of mercury was so sudden that the wave generated in the air was much shorter, and the "coup" was much more "sec," than that which was produced by a pistol charged with ordinary powder (pp. 47, 48, and pp. 278-281). He adds, "Il est encore difficile de décider si l'on a produit ainsi une onde unique, mais il est certain que si plusieurs ondes prennent naissance, elles doivent se suivre de très près" (p. 48).

Again, the observations of General H. L. Abbot (U.S. Engineers), incident to the heavy blastings at Hallet's Point, Hell Gate, in the harbour of New York, seem to render it at least probable that the waves transmitted by the earth reached the distant observers in groups, or as a train of waves (*Silliman's Journal*, vol. xv. (1878), p. 178 et seq.).

Sir G. B. Airy maintains that "there is reason to think that a single wave in air or in the medium of light would not produce the sensation of sound or colour" (*Undulatory Theory of Optics*, p. 15, art. 18, 1866). No reason is assigned for this somewhat extraordinary assertion. In the case of light, it is obviously impossible to experimentally test the validity of this idea of the former Astronomer Royal; and it does not appear to be sustained by the results of acoustical experiments.

correspondingly small. Hence, when the time of the blow or explosive impulse is exceedingly brief, the wave-length must be proportionately short.

17. *Application to Sound-Shadows.*—In the experiments of Colladon, if we assume that the brief shock of the hammer on a limited portion of the bell was alone transmitted to the distant observer, it is clear that only the short sound-waves thus generated would reach the distant obstructing wall or screen in the water; and consequently, the greater definiteness of the acoustical shadows in water as compared with those in air would be the necessary result of the greater shortness of the sound-waves in water. Under the foregoing assumptions, the theory of undulations appears to afford a satisfactory explanation of the phenomenon observed by Colladon. Nevertheless it would have been extremely interesting and instructive, as a very severe test of theory, had this distinguished physicist made observations on the relative distinctness of the sound-shadows in the water within the musical range of the submerged bell, as compared with those observed at points so remote that only the sharp blow of the hammer was audible in the water.

In like manner, the application of the principle of briefness of elastic-wave-genesis to the explanation of the phenomena observed by my son in his "Dynamite" experiments, is sufficiently obvious. In fact, all the phenomena incident to the explosion or detonation of the nitro-glycerine compounds indicate that the impulse generated is of indefinitely brief duration; indeed its suddenness is almost beyond conception. Thus, a dynamite cartridge placed upon a log of wood, unconfined and free, with nothing above it except the atmosphere, will, when exploding, shiver the portion of timber under it to atoms—the detonation being so instantaneous that the superincumbent air, as well as the gases generated, having no time to be displaced, become a veritable tampion.

The efficiency of surface-blasting under water by means of these explosive compounds, depends upon this extraordinary suddenness of detonation, which renders the effect akin to that of the sudden blow of an enormous unyielding mass. It is evident, that the wave generated in an elastic medium like water by an explosion of this character must be very intense and very short. Hence the acoustical shadow produced by an obstacle placed in its path of propagation must, as in the case of light, be sharply defined and definite in its boundaries. Thus the striking fact, that the protecting influence of the piles on the glass vessels plunged in the water was narrowly circumscribed within the limits of the geometrical shadow

may be rationally traced to the extreme shortness of the elastic wave, due to the inconceivably brief duration of action of the generative detonations. This view seems to afford a satisfactory explanation of the remarkable results revealed by the experiments in the harbour of San Francisco.

18. *Gunpowder Explosions*.—If the foregoing is the true explanation of the definiteness of the sound-shadows cast in the preceding experiments, then the waves generated by the explosion of ordinary gunpowder, being less sudden, should not produce as sharply-defined shadows as those due to the detonation of dynamite. We have, so far as known, no specific experiments testing this point; but it seems to be quite reasonable that such will be found to be the case whenever the test of experiment is applied; for it is well known that the subaqueous explosions of ordinary powder do not give rise to the remarkable concussions so characteristic of the detonations of the nitro-glycerine mixtures.

19. *Dynamite Explosions in Air*.—Moreover, if my explanation is correct, the acoustical shadows produced by nitro-glycerine detonation in air ought also to be more sharply defined than those due to sounds less suddenly generated. In other words, if the distinctness of sound-shadows depends upon the duration of the impulse which produces the accompanying sound-wave, then the definiteness of the shadows cast by sounds propagated through the air should vary with the suddenness of the action of the generating cause.

Inasmuch as the variations in the duration of the genesis of audible sounds in the atmosphere must, in ordinary experience, be very great, it may, at first sight, appear incredible that the corresponding differences in the perfection of sound-shadows cast by obstacles in the paths of different kinds of sounds should have escaped the most casual observation. But it must be recollected that, for the reasons already assigned (1), (2), (3) and (4), aerial acoustical shadows are not readily appreciated by the ear. Moreover, in the case of sounds transmitted by the air, the distinctness of such shadows is most seriously impaired by the numerous reflected waves which come from circumjacent objects. It should be borne in mind that it is only very recently (5) that the influence of acuteness of sounds on the distinctness of the resulting shadows has been satisfactorily verified by experiment. In like manner I venture to predict that careful experiments will verify the deduction that the shadows due to sounds generated by the extraordinarily brief detonations of dynamite are more sharply defined than those owing their origin to sounds less suddenly produced.

In confirmation of the foregoing view, the following observation may be cited : on the 16th of April, 1880, an explosion of about 2000 or 3000 pounds of a nitro-glycerine compound occurred at the "Giant Powder Works," situated under a bluff on the eastern shore of the Bay of San Francisco, at a distance (determined by triangulation) of 16,201 feet (4938 metres) in a direct line, in a north-west direction, from my room in the University building. About twenty-five adult men, a majority of them Chinamen, were literally blown to atoms, no one escaping to reveal the cause of the accident. The concussion at the University buildings—more than three miles distant—was sufficient to break about a dozen panes of stout window-glass on the side next to the explosive centre. Nearly every person about the University grounds experienced two distinct shocks—one transmitted by the air, and the other by the ground. The cottage occupied by my brother (Professor Joseph LeConte) was situated in the geometrical shadow of one of the buildings, being about 890 feet on the further side of it. No aerial shock was experienced by him or any member of the household ; and the concussion transmitted by the earth was alone felt as a shock emanating from the floor. In other terms, the acoustical shadow cast by the intervening structure completely cut off the sound-wave coming by the air. It is scarcely necessary to add, that for ordinary sounds such would not have been the result.

20. *Phenomenon of Jets*.—The singular phenomenon observed by my son (14), of numerous small jets projected from the surface of the water when the shock transmitted by the liquid reached the surface-area above the exploding cartridge, was probably due to the circumstance that when the short and intense elastic wave emerged in a direction normal, or nearly normal, to the aqueous surface, the tense superficial capillary film yielded to the sudden impulse more readily at some points than at others. The sensibly homogeneous character of such a tensile elastic film would naturally tend to group the points of rupture, or jets of water, into more or less perfect order, partaking more or less of geometrical symmetry. Hence the curious quincunx-like arrangement of jets as viewed by the observer near the water-level. According to this view, the phenomenon in question seems to find its counterpart or analogue in the more or less symmetrical forms produced by the intersection of the lines of rupture as the result of the tensional strains due to the contraction of homogeneous masses, during the process of cooling or of desiccation. Thus the columnar structure of certain igneous rocks seems to be due to the tensile stress of contraction by cooling after



solidification supervened ; while the analogous structure developed by the desiccation of homogeneous masses of moist clay, mud, or starch appears to be produced by a similar strain consequent upon shrinkage from loss of moisture. In a similar manner, the tense superficial capillary film of the water, when it experiences the sudden molecular impulse due to the emergence of the elastic pulse, is ruptured along lines more or less symmetrically disposed on the surface of the water ; and the liquid beneath is projected through these lines or points of least resistance.

Berkeley, California, Oct. 25, 1881.

XIII. *Chemical Symmetry, or the Influence of Atomic Arrangement on the Physical Properties of Compounds.* By THOMAS CARNELLEY, D.Sc., Professor of Chemistry in Firth College, Sheffield\*.

TWO years ago I published in this Magazine (Oct. 1879) a paper on the Influence of Atomic Weight, in which I endeavoured to trace the connexion between the atomic weights of the elements and their properties and those of their compounds. In the present paper I wish to consider this subject from a different point of view, viz. the influence which the atomic position or arrangement has on the properties of compounds.

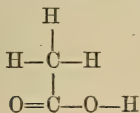
This is a subject which has lately absorbed a great deal of attention, more especially as regards the connexion between the refractive indices of compounds and the arrangement of their constituent atoms in the molecule ; and it will be my object to give as brief and as clear a sketch as possible of the chief results which have been obtained up to the present, tracing the influence which atomic arrangement has on (1) the melting-point, (2) the solubility, (3) the heat of formation, (4) the heat of combustion, (5) the action of polarized light, (6) the specific refraction, and (7) the tinctorial properties of chemical compounds. For this purpose I shall necessarily limit myself entirely to the consideration of carbon compounds, and to those which are isomeric with one another.

Those compounds are said to be isomeric which, though having the same percentage composition and the same molecular weight, have very different physical and chemical properties. This difference in properties must evidently depend on the different arrangement or linking together of atoms in the molecules of the several compounds. Thus, acetic acid

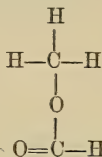
\* Communicated by the Author, being the Opening Address of the Session to the Owens College Chemical Society, Nov. 18, 1881.



and methyl formate have both exactly the same composition, viz.  $C_2H_4O_2$ , and yet have very different properties,—the former being a well-characterized acid, which on cooling solidifies in the form of large transparent plates, which melt at  $+17^\circ$  and boil at  $118^\circ C.$ , it possesses a pungent sour smell, and is highly corrosive; whilst the latter is a colourless liquid which has not yet been obtained in the solid state, and boils as low as  $33.4^\circ$ , or about  $85^\circ$  below the isomeric acetic acid, from which it also differs notably in emitting a pleasant ethereal smell. Since both compounds have exactly the same composition, this remarkable difference in properties can only be caused by the atoms being arranged differently in the two bodies; and that the atoms *are* differently arranged, we know from the various chemical decompositions which the two compounds undergo. This difference in atomic arrangement is represented by the following graphical formulæ:—



Acetic acid.



Methyl formate.

In the former the two carbon atoms are directly united, whilst in the latter they are combined indirectly by means of oxygen.

### I. INFLUENCE OF ATOMIC ARRANGEMENT ON THE MELTING-POINT.

It seems strange that scarcely any attempt has been made to trace the connexion between the composition and melting-points of carbon compounds, notwithstanding that the melting-points of a very large number of such compounds have been determined. The most noteworthy of these attempts is that of Baeyer, in regard to the melting-points of the fatty acids, and that of Körner, who states that, amongst aromatic compounds, what are called para-derivatives usually melt higher than the corresponding ortho- and meta-derivatives.

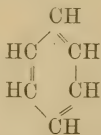
Attention has been directed almost exclusively to the boiling-points. Now the boiling-points are by no means so suitable for tracing the influence of atomic arrangement as the melting-points, since they are far from being such a fixed property as the latter; for, as is well known, the boiling-point is raised or lowered considerably by even small alterations in the pressure, whilst under ordinary circumstances the melting-

point of a pure compound is practically fixed and constant, and hence depends solely on the nature of the compound, whilst the boiling-point depends not only on the nature of the compound, but also on the superincumbent pressure; and, further, given alterations of pressure by no means produce corresponding alterations in the boiling-points of different compounds. It is therefore far easier to trace the connexion between melting-point and atomic arrangement than the connexion between boiling-point and atomic arrangement.

Such considerations as these induced me, about three years ago, to commence the study of the influence of composition and atomic arrangement on the melting-points of organic compounds. And for this purpose I have made complete lists of all the melting- and boiling-points which have been determined up to the present date. This tabulation has taken three years, and was finished only a few weeks ago. During this time I have collected not far short of 30,000 melting- and boiling-points, about one half of which are melting-points. The systematic arrangement of this enormous quantity of data is now in progress; and I have already been able to trace certain relations between them, which I hope will throw light on the influence of atomic arrangement. Some of these I now propose to describe; but at the same time I wish to say that, though these conclusions have been verified in a very large number of cases, I have not yet been able to test them in every possible case, because the systematic tabulation of my lists of melting-points is not yet completed.

Of the compounds of carbon, the aromatic compounds are perhaps the most important, and are certainly the most interesting. These compounds may all be considered as derived from benzene.

Benzene has the formula  $C_6H_6$ ; and its constitution is generally represented as follows:—

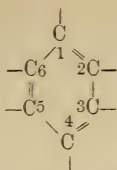


or it consists of a closed ring of six atoms of carbon united alternately with one and two combining-powers, whilst the fourth combining-power of each carbon atom is combined with hydrogen.

The aromatic compounds are derived from this ring by

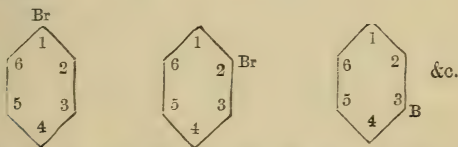
replacing one or more of the atoms of hydrogen by the atoms or groups of atoms of other elements.

The ring

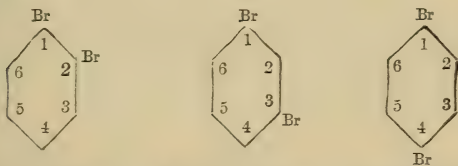


is called the benzene ring, or the benzene nucleus; and the carbon atoms in this ring we will number, for sake of distinction, as in the figure.

Now suppose we replace one atom of hydrogen by an atom of another element, say bromine; then we can only get one derivative, for an identical compound is obtained no matter which of the six atoms of hydrogen is replaced by the atom of bromine, thus:—



But when we replace two atoms of hydrogen by two like atoms of another element, or by two like groups of elements, then no less than three different isomeric bodies may be obtained; viz.—



Ortho- or 1.2-dibrom-  
benzene.

Meta- or 1.3-dibrom-  
benzene.

Para- or 1.4-dibrom-  
benzene.

It has been observed for some time past, that para-compounds always melt higher than ortho- and meta-compounds; whereas, as regards the ortho- and meta-compounds, the former sometimes melt higher, and sometimes lower, than the latter.

Now the arrangement of the atoms in the para-compounds is symmetrical, whilst in the ortho- and meta-compounds the

arrangement is asymmetrical; *i. e.* if we imagine the para-compound to be suspended from a point in the centre of the benzene ring, then the molecule would balance in any position, whilst this would not be the case with the ortho- and meta-compounds. Or, in other words, the centre of gravity of the molecule of the para-compounds corresponds more nearly with the centre of figure of the molecule than is the case with the ortho- and meta-compounds. This fact led me to conclude that a similar rule might hold good, not only with the primary derivatives of benzene, but also in the case of all isomeric compounds of carbon; and this appears to be true in a very large number of instances. I have therefore ventured to conclude, "*That of two or more isomeric compounds, those whose atoms are the MORE SYMMETRICALLY and the MORE COMPACTLY arranged melt higher than those in which the atomic arrangement is asymmetrical or in the form of long chains*"\*.

After working out this subject at some length, I noticed that Mr. Henry Watts had already observed, in the third Supplement of his well-known 'Dictionary of Chemistry,' that "the more symmetrical the constitution of a benzene derivative, the greater is the resistance which it offers to the passage from the solid to the liquid state," or, in other words, the higher the melting-point. Subsequently, however, in a note to a paper by Neville and Winther (Journ. Chem. Soc. xxxvii. p. 450), Mr. Watts emphatically says that he intended this rule to apply only and solely to the derivatives of benzene containing but six atoms of carbon; whilst I believe that it holds good, with a very few exceptions, in the case of all carbon compounds whatever.


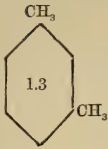
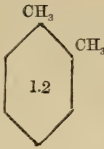

Let us now illustrate this rule by a number of examples taken almost at random. In the following tables the compounds are generally, though not always, arranged in the order of symmetry, those to the left being the most symmetrical. In the case where two compounds are equally symmetrical, that which is most compact is placed to the left.

## I.

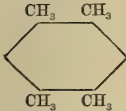

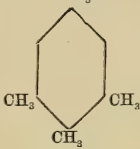
Tetramethyl methane.	Normal pentane.	Dimethylethyl methane.
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\   \\ \text{CH}_3 \end{array}$	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_2 \cdot \text{CH}_3 \\ \diagdown \quad / \\ \text{C} \\ / \quad \diagdown \\ \text{CH}_3 \quad \text{H} \end{array}$
m.p. = -20.	Liquid.	Liquid.


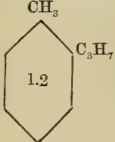
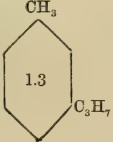
\* In the examples given below of this and of all the rules stated subsequently, the exceptions are in every case marked with an asterisk.

II.

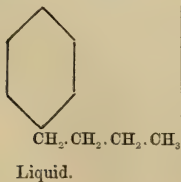
	Dimethyl benzene.		Ethyl benzene.
			
1.4	1.3	1.2	
m.p. = 15.	= 2.	below -22.	Liquid.

III.

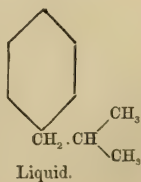
Durene.	1.4 Diethyl benzene.	Isodurene.	Dimethylethyl benzene.
			
m.p. = 80.	Liquid.	Liquid.	$C_6H_3 \cdot (CH_3)_2 \cdot C_2H_5$

Methylpropyl benzene.		Methylisopropyl benzene.
		
1.4	1.2	1.3
Liquid.	Liquid.	Liquid.

Normal butyl benzene.



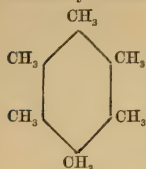
Isobutyl benzene.





## IV.

Hexamethyl benzene.



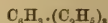
m.p. = 150.

Dipropyl benzene.



Liquid.

Triethyl benzene.



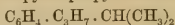
Liquid.

Amylmethyl benzene.



Liquid.

Propylisopropyl benzene.



Liquid.

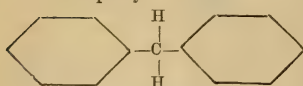
Hexyl benzene.



Liquid.

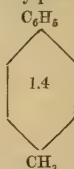
## V.

Diphenyl methane.



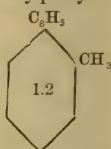
m.p. = 26.5.

Tolylphenyl.



m.p. = -2.

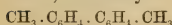
Tolylphenyl.



Liquid.

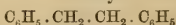
## VI.

1.4; 1.4 Ditolyl.



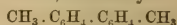
m.p. = 121.

Dibenzyl.



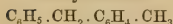
m.p. = 52.

1.2; 1.4 Ditolyl.



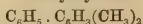
Liquid.

Benzyltoluene.



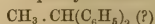
Liquid.

Phenylxylene.



Liquid.

Diphenyl ethane.



Liquid.

## VII.

Derivatives of Ethane.

	XX.
Dibromide . . . . .	Br . Br
Diiodide . . . . .	I . I
Chloroiodide . . . .	Cl . I
Bromoiodide . . . .	Br . I
Diphenide . . . . .	Ph . Ph
Sulphide . . . . .	S''
Iodopropionic acid	COOH . I
Succinic acid . . . .	COOH . COOH




Ethylene.	Ethylidene.
$\text{XH}_2\text{C} - \text{CH}_2\text{X}$	$\text{H}_3\text{C} - \text{CHX}_2$
m.p. = 9	Liquid.
73	"
Solid in freezing-mixture.	"
m.p. = 28	"
52 (dibenzyl)	"
112	95
82	Liquid.
180	129

## VIII.


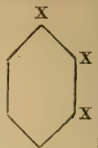

		XHC=CHX.	H <sub>2</sub> C=CX <sub>2</sub> .
Diphenide . . . . .	Ph . Ph	120 (stilbene)	Liquid.
Ditolide . . . . .	C <sub>7</sub> H <sub>7</sub> . C <sub>7</sub> H <sub>7</sub>	{ 176 (dimethyl stilbene) }	Liquid.

## IX.

*Derivatives of Benzene.*

		Para X  1.4 X	Meta X  1.3 X	Ortho X  1.2 X
Dichlorobenzene . . . . .	Cl . Cl	53	L at -18	L at -14
Dibromobenzene . . . . .	Br . Br	89	-28	-1
Diiodobenzene . . . . .	I . I	127	40	94
Dicyanobenzene . . . . .	CN . CN	222	158	
Chloriodobenzene . . . . .	Cl . I	56	...	L
Bromiodobenzene . . . . .	Br . I	92	L	L
Dihydroxybenzene . . . . .	OH . OH	172	99	112
Disulphydrobenzene . . . . .	SH . SH	98	27	
Dinitrobenzene . . . . .	NO <sub>2</sub> . NO <sub>2</sub>	171	90	118
Diamidobenzene . . . . .	NH <sub>2</sub> . NH <sub>2</sub>	140	63	99
Nitrobromobenzene . . . . .	NO <sub>2</sub> . Br	126	56	41.5
Nitrochlorobenzene . . . . .	NO <sub>2</sub> . Cl	83	44	32
Nitriodobenzene . . . . .	NO <sub>2</sub> . I	171	36	49
Amidobromobenzene . . . . .	NH <sub>2</sub> . Br	64	18	31
Amidochlorobenzene . . . . .	NH <sub>2</sub> . Cl	70	L	Labove -14
Amidiodobenzene . . . . .	NH <sub>2</sub> . I	60	25	
Amidonitrobenzene . . . . .	NH <sub>2</sub> . NO <sub>2</sub>	146	110	71
Dimethylbenzene . . . . .	CH <sub>3</sub> . CH <sub>3</sub>	15	L	L
Diphenylbenzene . . . . .	Ph . Ph	205	1.3 or 1.2 L	L
Tolyldipenylmethane . . . . .	Me . (CHPh <sub>2</sub> )	71	59.5 or L	L or 59.5
Methyl chlorobenzene . . . . .	Me . Cl	6.5	L	L
Methyl bromobenzene . . . . .	Me . Br	28	L	L
Methyl iodobenzene . . . . .	Me . I	35	L	L
Methyl amidobenzene . . . . .	Me . NH <sub>2</sub>	45	L	L
Phenyl chlorobenzene . . . . .	Ph . Cl	75	...	4
Phenyl bromobenzene . . . . .	Ph . Br	89	...	L
Phenyl amidobenzene . . . . .	Ph . NH <sub>2</sub>	50	...	48
Di-(amidomethyl)benzene . . . . .	(CH <sub>2</sub> . NH <sub>2</sub> )(CH <sub>2</sub> . NH <sub>2</sub> )	99	89	
Hydroxy-carboxyl benzene . . . . .	OH . COOH	210	200	156
Methoxy-carboxylbenzene . . . . .	OCH <sub>3</sub> . COOH	175	106	99
Ethoxy-carboxylbenzene . . . . .	OEt . COOH	195	137	20
Fluo-carboxyl benzene . . . . .	F . COOH	182	123	
Chloro-carboxyl benzene . . . . .	Cl . COOH	234	152	137
Bromo-carboxyl benzene . . . . .	Br . COOH	250	155	148
Iodo-carboxyl benzene . . . . .	I . COOH	267	185	159
Hydroxy-potassium-sul- phobenzene . . . . . }	OH . SO <sub>3</sub> K	not at 260	200	240
Bromhydroxybenzene . . . . .	OH . Br	64	32	L
Nitro-carboxyl benzene . . . . .	COOH . NO <sub>2</sub>	240	141	143
Amido-carboxyl benzene . . . . .	COOH . NH <sub>2</sub>	187	174	144

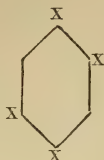
## X. Triderivatives of Benzene.

		Symmetrical.	Consecutive.	Asymmetrical
		 1. 3. 5	 1. 2. 3	 1. 2. 4
Trichlorobenzene .....	Cl. Cl. Cl	64	54	16
Tribromobenzene .....	Br. Br. Br	119	87	44
Methyl dibromobenzene	CH <sub>3</sub> . Br. Br	39	27	L
Nitrodibromobenzene {	NO <sub>2</sub> . Br. Br.	104	...	62
	Br. Br. NO <sub>2</sub>	...	59	...
	Br. NO <sub>2</sub> . Br	...	83	85
Nitrodichlorobenzene {	NO <sub>2</sub> . Cl. Cl	65	...	32
	Cl. Cl. NO <sub>2</sub>	...	...	43
	Cl. NO <sub>2</sub> . Cl	...	...	55
Nitrochlorobromoben- zene ... ..	NO <sub>2</sub> . Cl. Br	83	...	47
	Cl. NO <sub>2</sub> . Br	...	...	69
	Br. NO <sub>2</sub> . Cl	...	...	50
Amidodibromobenzene {	NH <sub>2</sub> . Br. Br	57*	...	79
	Br. NH <sub>2</sub> . Br	...	...	52
	Br. Br. NH <sub>2</sub>	...	...	80
Amidodichlorobenzene {	NH <sub>2</sub> . Cl. Cl	51*	24	63
	Cl. NH <sub>2</sub> . Cl	...	...	50
	Cl. Cl. NH <sub>2</sub>	...	...	71
Dibrombenzoic acid ...	COOH. Br. Br	209	...	...
	Br. Br. COOH	...	...	228*
	Br. COOH. Br	...	...	151
Dinitrobenzoic acid ...	COOH. NO <sub>2</sub> . NO <sub>2</sub>	205	...	179
	NO <sub>2</sub> . COOH. NO <sub>2</sub>	...	202	140

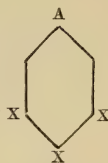
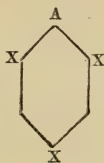
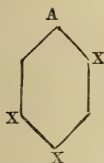
## XI. Tetraderivatives of Benzene.

Order of symmetry.		m.p.	1.	2.	3.	4.	5.	6.
{ 1.	Br. Br. Br. Br	138	Br	Br	...	Br	Br	
{ 2.	" " " "	99	Br	...	Br	Br	Br	
{ 1.	Cl. Cl. Cl. Cl	138	Cl	Cl	...	Cl	Cl	
{ 2.	" " " "	50	Cl	...	Cl	Cl	Cl	
{ 3.	" " " "	46	Cl	Cl	Cl	Cl		
{ 1.	NH <sub>2</sub> . Br. NO <sub>2</sub> . Br	202	NH <sub>2</sub>	Br	...	NO <sub>2</sub>	...	Br
{ 2.	" " " "	127	NH <sub>2</sub>	Br	...	Br	...	NO <sub>2</sub>
{ 1.	NH <sub>2</sub> . Cl. Cl. NO <sub>2</sub>	100	NH <sub>2</sub>	Cl	...	NO <sub>2</sub>	...	Cl
{ 2.	" " " "	66	NH <sub>2</sub>	Cl	...	NO <sub>2</sub>	Cl	NO <sub>2</sub>
{ 1.	CH <sub>3</sub> . Cl. Cl. Cl	138	CH <sub>3</sub>	Cl	...	...	Cl	
{ 2.	" " " "	27-35	CH <sub>3</sub>	...	Cl	Cl	Cl	
{ 3.	" " " "	46*	CH <sub>3</sub>	Cl	Cl	Cl	Cl	
{ 1.	CH <sub>3</sub> . Br. Br. Br	112	CH <sub>3</sub>	Br	...	Br	Br	
{ 2.	" " " "	88	CH <sub>3</sub>	...	Br	Br	Br	Br
{ 3.	" " " "	66	CH <sub>3</sub>	Br	...	Br		
{ 4.	" " " "	59	CH <sub>3</sub>	Br	Br	...	...	Br
{ 5.	" " " "	52	CH <sub>3</sub>	Br	Br	...	Br	
{ 6.	" " " "	44	CH <sub>3</sub>	Br	Br	Br		

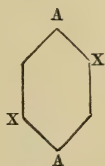
*Note.*—When all the side chains are of one kind the form



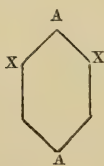
is the most symmetrical, and always has the highest melting-point. But when the side chains are not all of the same kind, then there seems to be a struggle between the three forms



and between

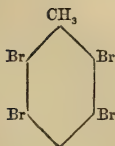


and

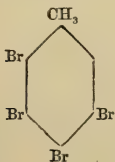


## XII.

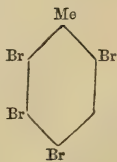
### *Pentaderivatives of Benzene.*



m.p. = 116.

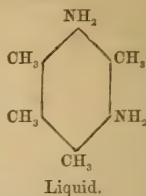
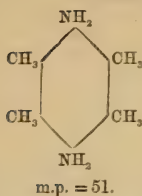


m.p. = 111.

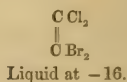
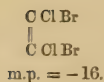


m.p. = 107.

## XIII.

*Hexaderivatives of Benzene.*

## XIV.



## XV.



X=Cl m.p. = 6.5  
X=Br m.p. = 28  
X=I m.p. = 35



Liquid.  
Liquid.  
Liquid.



Liquid.  
Liquid.  
Liquid.



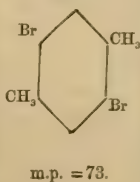
Liquid.  
Liquid.  
Liquid.

## XVI.

Tolylene dibromide.



Dibromparaxylylene.



Dibromometaxylylene.

?

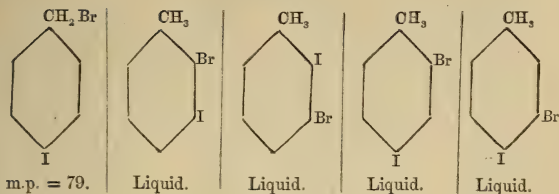
m.p. = 69.

Cinnamene dibromide.

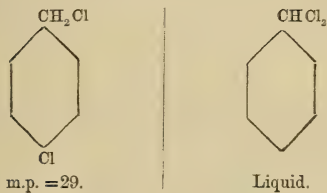




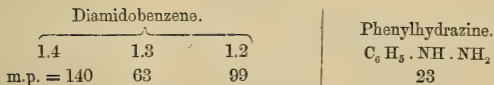
XVII.



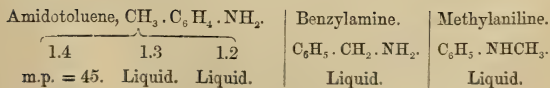
XVIII.



XIX.

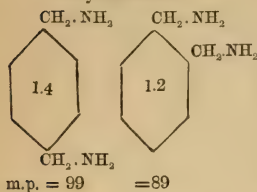


XX.

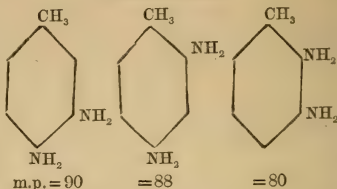
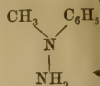


## XXI.

Tolylenediamine.



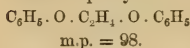
Diamidotoluene.

Phenylmethy-  
hydrazine.

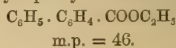
Liquid.

## XXII.

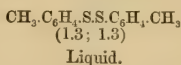
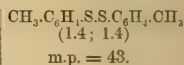
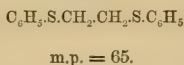
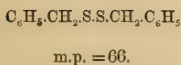
Ethenediphenylether.



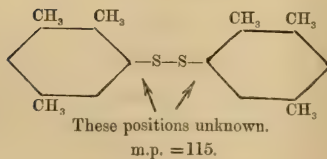
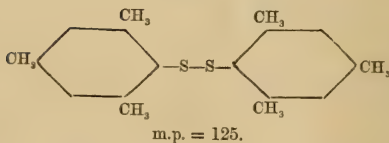
Ethyldiphenyl carbonate (1.4).



## XXIII.

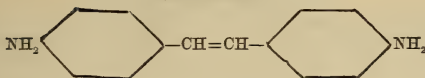


## XXIV.



XXV.

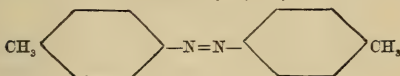
Diamidostilbene.



m.p. = 170\*.

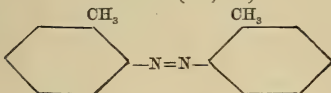
\* This, though nearly, is not quite so symmetrical as (1.4; 1.4) azotoluene.

Azotoluene (1.4; 1.4).



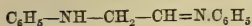
m.p. = 144.

Azotoluene (1.2; 1.2).



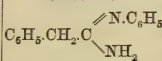
m.p. = 137.

Ethenyldiphenylamidine.



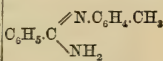
m.p. = 132.

Phenylacetophenyl-  
amidine.



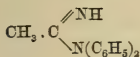
m.p. = 128.

Benzenyltolylamidime.



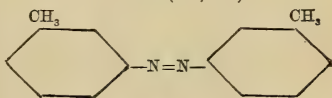
m.p. = 99.

Ethenylisodiphenylamidine.



m.p. = 63.

Azotoluene (1.3; 1.3).



m.p. = 54.

The influence of symmetry on the melting-point is still further shown by the following table, which contains the melting-points of the *most* symmetrical modification of a few of the mono-, di-, tri-, tetra-, penta-, and hexa-derivatives of benzene; from which it will be seen that the melting-points of the mono- and penta-derivatives are comparatively always very low, whilst those of the other derivatives are high; the reason being that benzene cannot form symmetrical mono- and penta-derivatives, whereas a symmetrical form of a di-, tri-, tetra-, and hexa-derivative is always possible.

	Ben- zene.	Mono- deriva- tive.	Di- deriva- tive.	Tri- deriva- tive.	Tetra- deriva- tive.	Penta- deriva- tive.	Hexa- deriva- tive.
Position of side chains...	0	1	1.4	1.3.5	1.2.4.5	1.2.3.4.5	1.2.3.4.5.6
The side chains being—							
CH <sub>3</sub> .....	7	Liquid	15	Liquid	80	50	164
Cl .....	7	Liquid at -40	53	63.5	138	74	226
Br .....	7	b. -20	89	119	140	a 240	a 310
I .....	7	Liquid	127				
NO <sub>2</sub> .....	7	Liquid	171				
NH <sub>2</sub> .....	7	-8	147				

*Influence of Compactness, or number of Side Chains on the  
Melting- and Boiling-points.*

Lothar Meyer has pointed out, in his 'Modern Theories of Chemistry,' p. 280, "*that, of any number of isomeric compounds, those are the most volatile in which there are the greatest number of side chains, or in which the main chain of atoms is most branched, and therefore in which the main chain is the shortest.*"

From the observation of a great number of compounds, I cannot help concluding that a rule the exact reverse of the above holds good as regards the melting-point, viz. *that those isomeric compounds melt the highest in which there are the greatest number of side chains.* This has already been indicated to some extent above, where it has been pointed out that the greater the compactness of the molecule the higher the melting-point. The above rules may be illustrated as follows:—

	Boiling- point.	Melting- point.
Pentanes. { <div style="display: inline-block; vertical-align: middle; margin-left: 10px;"> <math>\begin{array}{l} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \text{ .....} \\ \text{CH}_3 \diagup \text{CHCH}_2\text{CH}_3 \text{ .....} \\ \text{CH}_3 \end{array}</math> </div>	38	Liquid.
	30	Liquid.
{ <div style="display: inline-block; vertical-align: middle; margin-left: 10px;"> <math>\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}-\text{CH}_3 \\   \\ \text{CH}_3 \end{array}</math> </div>	9.5	-20
Octanes. { <div style="display: inline-block; vertical-align: middle; margin-left: 10px;"> <math>\begin{array}{l} \text{CH}_3-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\ \text{CH}_3 \diagup \text{CH}-\text{CH}_2\text{CH}_2-\text{CH} \diagdown \text{CH}_3 \text{ .....} \\ \text{CH}_3 \end{array}</math> </div>	125	Liquid.
	108	Liquid.
{ <div style="display: inline-block; vertical-align: middle; margin-left: 10px;"> <math>\begin{array}{c} \text{CH}_3\text{CH}_3 \\   \quad   \\ \text{CH}_3-\text{C}-\text{C}-\text{CH}_3 \text{ .....} \\   \quad   \\ \text{CH}_3\text{CH}_3 \end{array}</math> </div>	105	96-97

Table (continued).

	Boiling-point.	Melting-point.
Pentyl alcohols, $\left\{ \begin{array}{l} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \dots\dots\dots \\ \text{CH}_3\text{CHCH}_2\text{CH}_2\text{OH} \dots\dots\dots \\ \quad \text{CH}_3 \\ \text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_3 \dots\dots\dots \\ \quad \text{OH} \\ \quad \text{CH}_3 \\ \text{CH}_3-\text{C}-\text{OH} \dots\dots\dots \\ \quad \text{CH}_3 \end{array} \right.$	117 109  97  84	Liquid. Liquid.  Liquid.  25
Heptyl chlorides, $\left\{ \begin{array}{l} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} \dots\dots\dots \\ \text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CHCH}_3 \dots\dots\dots \\ \quad \text{CH}_3 \qquad \qquad \text{Cl} \\ \quad \text{CH}_3 \quad \text{CH}_3 \\ \text{CH}_3-\text{C}-\text{C}-\text{Cl} \dots\dots\dots \\ \quad \text{CH}_3 \quad \text{CH}_3 \end{array} \right.$	159 136   .....	Liquid. Liquid.   136
Butyric acids, $\left\{ \begin{array}{l} \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} \dots\dots\dots \\ \text{CH}_3\text{CHCOOH} \dots\dots\dots \\ \quad \text{CH}_3 \end{array} \right.$	162 154	0 L (?)*
Valeric acids, $\left\{ \begin{array}{l} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH} \dots\dots\dots \\ \text{CH}_3\text{CHCH}_2\text{COOH} \dots\dots\dots \\ \quad \text{CH}_3 \\ \text{CH}_3\text{CH}_2\text{CHCOOH} \dots\dots\dots \\ \quad \text{CH}_3 \\ \quad \text{CH}_3 \\ \text{CH}_3-\text{C}-\text{COOH} \dots\dots\dots \\ \quad \text{CH}_3 \end{array} \right.$	184 175  173  164	Liquid. Liquid.  Liquid.  35.4
Butyl cyanides, $\left\{ \begin{array}{l} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CN} \dots\dots\dots \\ \text{CH}_3\text{CHCH}_2\text{CN} \dots\dots\dots \\ \quad \text{CH}_3 \\ \quad \text{CH}_3 \\ \text{CH}_3-\text{C}-\text{CN} \dots\dots\dots \\ \quad \text{CH}_3 \end{array} \right.$	140 127   105	Liquid. Liquid.   15-16



Table (continued).

	Boiling-point.	Melting-point.
Dipropargyl, $\text{CH}\equiv\text{C}-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{CH}$	85	Liquid.
Benzene, $\begin{array}{c} \text{HC} \quad \text{CH}=\text{CH} \\ \parallel \quad \diagup \quad \diagdown \\ \text{HC} \quad \text{CH} \quad \text{CH} \end{array}$ .....	81	7
Amyl benzene, $\text{C}_6\text{H}_5.\text{CH}_2.\text{CH}_2.\text{CH} \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{CH}_3 \end{array}$ ...	193	Liquid.
Propyldimethyl benzene, $\left. \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_2.\text{CH}_2.\text{CH}_3 \end{array} \right\} \text{C}_6\text{H}_5$ ...	188	Liquid.
Diethylmethyl benzene, $\text{C}_6\text{H}_5 \left\{ \begin{array}{l} \text{CH}_2.\text{CH}_3 \\ \text{CH}_2.\text{CH}_3 \\ \text{CH}_3 \end{array} \right.$ { 178 198-200 }	{ 178 198-200 }	Liquid.
Pentamethyl benzene, $\text{C}_6\text{H} \left\{ \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \end{array} \right.$ .....	225*	50

	Melting-point.		Melting-point.
Propyl terephthalate	31°	and Isopropyl terephthalate	56°
Butyl	„	Liquid, and Isobutyl	„
Butyl hippurate	40·5,	and Isobutyl hippurate	45·5

So great indeed is the influence of the compactness of the molecule, that it sometimes overbalances the influence of increase of atomic weight : thus

		Melting-point.
Methyl terephthalate	$\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{COO}.\text{CH}_3 \\ \diagdown \text{COO}.\text{CH}_3 \end{array}$ .....	140
Ethyl	„ $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{COO}.\text{CH}_2.\text{CH}_3 \\ \diagdown \text{COO}.\text{CH}_2.\text{CH}_3 \end{array}$ .....	44
Propyl	„ $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{COO} \text{CH}_2.\text{CH}_2.\text{CH}_3 \\ \diagdown \text{COO} \text{CH}_2.\text{CH}_2.\text{CH}_3 \end{array}$ ...	31
Butyl	„ $\text{C}_6\text{H}_4 \begin{array}{l} \diagup \text{COO} \text{CH}_2.\text{CH}_2.\text{CH}_2.\text{CH}_3 \\ \diagdown \text{COO} \text{CH}_2.\text{CH}_2.\text{CH}_2.\text{CH}_3 \end{array}$	Liquid.

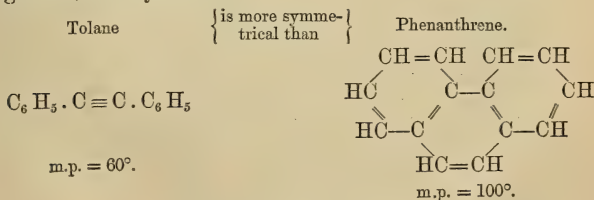
		Melting-point.
Methyl hippurate	$(C_8H_8NO).COO.CH_3$ .....	80·5
Ethyl	„ $(C_8H_8NO).COO.CH_2.CH_3$ .....	60·5
Butyl	„ $(C_8H_8NO).COO.CH_2.CH_2.CH_2.CH_3$	40·5

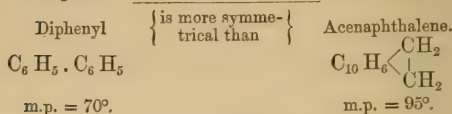
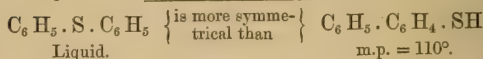
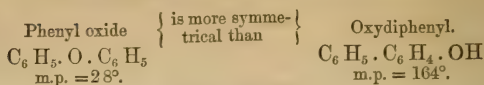
Isobutyl hippurate  $(C_8H_8NO).COO.CH_2.CH \begin{smallmatrix} \swarrow CH_3 \\ \searrow CH_3 \end{smallmatrix}$  ... 45·5

Isoamyl „  $(C_8H_8NO).COO.CH_2.CH_2.CH \begin{smallmatrix} \swarrow CH_3 \\ \searrow CH_3 \end{smallmatrix}$  27·5

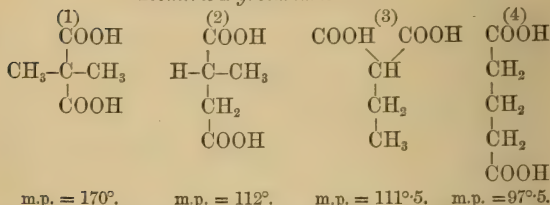
It will now be necessary to make a few remarks in regard to the examples which have been given in illustration of what is thought to be a true connexion between atomic structure and melting-point, and more especially as regards the influence of symmetry. It would, of course, be easy to support any theory if we merely gave those examples which were favourable and excluded all those which were adverse. This, however, has not been done in the examples which have been given above. For the purpose of this paper there were taken quite at random somewhere about 300 cases to which the rule of symmetry could be applied; and of these 278 were in agreement with the rule, whilst 22 were exceptions; the latter amounted therefore to only 7 per cent., which proves that the rule is of almost general application. Many of the exceptions may possibly be due to the constitution or arrangement of the atoms not having been correctly determined, and might thus on close examination be shown to agree with the rule.

The following are some of the most marked exceptions included in the above 22, and which are undoubtedly real exceptions, since the constitution is known with a considerable degree of certainty:—





*Isomeric Pyrotartaric Acids.*



No. 4, which is more symmetrical than No. 2 and No. 3, is less compact; and perhaps this is the cause of the low melting-point.

Bäyer has shown that, if we compare the melting-points of homologous series, we find that the melting-point is materially influenced by odd and even numbers, in such a way that those compounds containing an even number of carbon atoms melt higher than the neighbouring compounds containing an odd number, thus:—

	Melting-point.			Melting-point.	
	Even.	Odd.		Even.	Odd.
$CH_2O_2$	...	8.6	$C_2H_2O_4$	200	
$C_2H_4O_2$	+17		$C_3H_4O_4$	...	132
$C_3H_6O_2$	...	b. -21	$C_4H_6O_4$	180	
$C_4H_8O_2$	+1		$C_5H_8O_4$	...	97
$C_5H_{10}O_2$	...	b. -16	$C_6H_{10}O_4$	148	
$C_6H_{12}O_2$	-2		$C_7H_{12}O_4$	...	103
$C_7H_{14}O_2$	...	-10.5	$C_8H_{14}O_4$	140	
$C_8H_{16}O_2$	+16		$C_9H_{16}O_4$	...	106
$C_9H_{18}O_2$	...	+12	$C_{10}H_{18}O_4$	127	
$C_{10}H_{20}O_2$	+30		$C_{11}H_{20}O_4$	...	108
<hr/>			<hr/>		
$C_{16}H_{32}O_2$	+62		$C_{17}H_{32}O_4$	...	132
$C_{17}H_{34}O_2$	...	+60			
$C_{18}H_{36}O_2$	+69				

[To be continued].

XIV. *The Beats of Mistuned Consonances.*

*To the Editors of the Philosophical Magazine and Journal.*

GENTLEMEN,

I HAVE just seen Prof. Silvanus Thompson's Note in your January Number. I have no books with me; but I think I can close the controversy, as far as I am concerned, without them.

As to the word "subjective," I am quite content to have Prof. Helmholtz and his translator (Mr. Ellis) as authorities for my use of it; and I fear I shall require some further authority before I shall feel called upon to give up a use now well established, sanctioned by custom and by the highest authorities.

As to the law that the beats of mistuned consonances of the form  $h : 1$  consist of variations of the lower note, (the law is not true for imperfect consonances in general,) no doubt I expressed myself hastily, and, as was evident, without referring to Kœnig's papers.

Notwithstanding this, I cannot admit that the citations made by Prof. Silvanus Thompson contain any demonstration of the law in question, though undoubtedly the last quotation contains a suggestion of the law. I must point out that the sentence translated by Prof. Silvanus Thompson is not quite correctly given; the preceding qualifying clause showing that it is only an assumption, not a definite conclusion. Further, there is no such experimental establishment of the law as to amount to a demonstration.

I have in fact recently learned, through a private source, that Kœnig had, some time ago, convinced himself of this result. But the experiments which were shown to my informant all bore the character of beats still associated with variations of the upper note; and my informant, a most competent person, was wholly unable to verify the conclusion. This agrees entirely with my own observations made with similar means. I therefore consider that the quotations from Kœnig made by Prof. Thompson contain nothing but assumption or inference on this point; and, indeed, they do not purport to be more.

I consider that, in my experiments, the disturbing effects of the harmonics are entirely separated out, so that direct demonstration of the law in question is obtained.

Yours truly,

R. H. M. BOSANQUET.

XV. *On the Theoretic Determination of Vapour-pressure and the Volumes of Vapour and Liquid.* By Prof. R. CLAUSIUS\*.  
(*Second Paper*†.)

§ 1. **I**N the first paper on this subject, I formed for the determination of the pressure of a gas as a function of the temperature and volume the following equation, which is a generalization of that which I had previously employed for carbonic acid:—

$$\frac{p}{RT} = \frac{1}{v-\alpha} - \frac{27(\alpha+\beta)}{8\theta(v+\beta)^2} \cdot \cdot \cdot \cdot (1)$$

Herein  $p$  denotes the pressure,  $v$  the volume, and  $T$  the absolute temperature—namely the sum  $273+t$ , if  $t$  represents the temperature reckoned from the usual zero-point. Further,  $R$  is the constant which already occurs in the usual expression of Mariotte and Gay-Lussac's law; and  $\alpha$  and  $\beta$  represent two other constants, the sum of which will further on be denoted by  $\gamma$ .  $\theta$  signifies a temperature-function which for  $T=0$  has the value 0, and for the critical temperature the value 1, but otherwise is provisionally to be left undetermined.

It is self-evident that we can give this equation a simpler form if we combine the temperature-function with the constant factors occurring in the term into one symbol. Namely, if we put

$$\Theta = \frac{8\theta}{27(\alpha+\beta)} = \frac{8\theta}{27\gamma}, \cdot \cdot \cdot \cdot (2)$$

the equation is changed into

$$\frac{p}{RT} = \frac{1}{v-\alpha} - \frac{1}{\Theta(v+\beta)^2} \cdot \cdot \cdot \cdot (3)$$

The relation between the temperature-function  $\Theta$  in this equation and that employed above,  $\theta$ , becomes particularly evident when it is borne in mind that the value assumed by  $\Theta$  for the critical temperature, and which may be denoted by  $\Theta_c$ , is to be determined by putting the value 1 for  $\theta$  in equation (2). Thence, namely, we get

$$\Theta_c = \frac{8}{27\gamma}; \cdot \cdot \cdot \cdot (4)$$

\* Translated from a separate impression, communicated by the Author, from Wiedemann's *Annalen*, 1881, vol. xiv. pp. 692-704.

† For the first paper see Wiedemann's *Annalen*, xiv. p. 279; translated in the 'Philosophical Magazine' for December 1881, vol. xii. p. 381.



and in consequence of this we can write

$$\theta = \frac{\Theta}{\Theta_c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In applying equation (1) to saturated vapour, the pressure of the saturated vapour was denoted by  $P$ , and the fraction  $P/RT$  by  $\Pi$ . The volumes of the saturated vapour and the liquid standing under the same pressure were denoted, in the usual manner, by  $s$  and  $\sigma$ ; but for the differences  $s - \alpha$  and  $\sigma - \alpha$  the simplified symbols  $W$  and  $w$  were introduced. In order to determine the quantities  $\Pi$ ,  $W$ , and  $w$  in their dependence on  $\theta$ , first all four quantities were expressed as functions of  $\lambda = \log(W/w)$ ; and then, to facilitate the further calculations, a table was added, from which for every value of  $\theta$  the corresponding value of  $\lambda$  can be taken. At the same time I remarked that, after the calculation of the table for  $\lambda$ , there would be little further difficulty in calculating a similar table for  $\Pi$ ,  $W$ , and  $w$  also; this I take leave to communicate *infra*:—

$\theta = \frac{\Theta}{\Theta_c}$	$\frac{\Pi}{\Pi_c}$	$\Delta$	$\frac{W}{W_c}$	$\Delta$	$\frac{w}{w_c}$	$\Delta$
0.20	0.0000059		672780		0.033767	
0.21	0.0000126	67	317340	355440	0.035714	1947
0.22	0.0000249	123	160680	156660	0.037692	1978
0.23	0.0000462	213	16505	74175	0.039700	2008
0.24	0.0000814	352	49140	37365	0.041740	2040
0.25	0.0001367	553	29263	19877	0.043812	2072
0.26	0.0002201	834	18166	11097	0.045918	2106
0.27	0.0003416	1215	11702	6464	0.048059	2141
0.28	0.0005131	1715	7789.7	3912.3	0.050235	2176
0.29	0.0007483	2352	5329.9	2449.8	0.052448	2213
0.30	0.0010627	3144	3758.3	1581.6	0.054701	2253
0.31	0.0014738	4111	2708.6	1049.7	0.056991	2290
0.32	0.0020002	5264	1994.6	714.0	0.059321	2330
0.33	0.0026621	6619	1497.4	497.2	0.061695	2374
0.34	0.0034808	8187	1144.2	353.2	0.064113	2418
0.35	0.0044780	9972	888.41	255.79	0.066575	2462
0.36	0.0056763	11983	699.97	188.44	0.069083	2508
0.37	0.0070987	14224	558.90	141.07	0.071638	2555
0.38	0.0087680	16693	451.73	107.17	0.074245	2607
0.39	0.010703	19380	369.24	82.49	0.076903	2658
0.40	0.012936	2230	304.94	64.20	0.079612	2709
0.41	0.015479	2543	254.25	50.69	0.082379	2767
0.42	0.018356	2877	213.84	40.41	0.085201	2822
0.43	0.021589	3233	181.30	32.54	0.088084	2883
0.44	0.025193	3604	154.87	26.43	0.091028	2944
0.45	0.029187	3994	133.22	21.65	0.094037	3009
0.46	0.033589	4402	115.34	17.88	0.097112	3075
0.47	0.038413	4824	100.45	14.89	0.10026	3148
0.48	0.043680	5267	87.953	12.497	0.10347	321

Table (continued).

$\theta = \frac{\theta}{\theta_c}$	$\frac{\Pi}{\Pi_c}$	$\Delta$	$\frac{W}{W_c}$	$\Delta$	$\frac{w}{w_c}$	$\Delta$
0.48	0.043680		87.953		0.10347	
0.49	0.049398	5718	77.421	10.532	0.10676	329
0.50	0.055577	6179	68.476	8.945	0.11013	337
0.51	0.062232	6655	60.836	7.640	0.11358	345
0.52	0.069372	7140	54.275	6.561	0.11712	354
0.53	0.077004	7632	48.612	5.663	0.12074	362
0.54	0.085139	8135	43.698	4.914	0.12445	371
0.55	0.093783	8644	39.414	4.284	0.12826	381
0.56	0.10294	9157	35.664	3.750	0.13217	391
0.57	0.11261	967	32.369	3.295	0.13619	402
0.58	0.12281	1020	29.460	2.909	0.14031	412
0.59	0.13353	1072	26.884	2.576	0.14456	425
0.60	0.14478	1125	24.595	2.289	0.14893	437
0.61	0.15657	1179	22.549	2.046	0.15340	447
0.62	0.16887	1230	20.720	1.829	0.15803	463
0.63	0.18171	1284	19.078	1.642	0.16279	476
0.64	0.19508	1337	17.700	1.478	0.16770	491
0.65	0.20899	1391	16.265	1.335	0.17277	507
0.66	0.22343	1444	15.056	1.209	0.17801	524
0.67	0.23837	1494	13.958	1.098	0.18341	540
0.68	0.25385	1548	12.960	.998	0.18891	560
0.69	0.26985	1600	12.049	.911	0.19479	578
0.70	0.28637	1652	11.217	.832	0.20079	600
0.71	0.30340	1703	10.454	.763	0.20702	623
0.72	0.32094	1754	9.7533	.7007	0.21347	645
0.73	0.33900	1806	9.1086	.6447	0.22019	672
0.74	0.35755	1855	8.5140	.5946	0.22717	698
0.75	0.37661	1906	7.9646	.5494	0.23445	728
0.76	0.39617	1956	7.4561	.5085	0.24204	759
0.77	0.41621	2004	6.9844	.4717	0.24997	793
0.78	0.43672	2051	6.5467	.4377	0.25827	830
0.79	0.45772	2100	6.1389	.4078	0.26697	870
0.80	0.47919	2147	5.7588	.3801	0.27612	915
0.81	0.50115	2196	5.4034	.3554	0.28573	961
0.82	0.52357	2242	5.0711	.3323	0.29587	1014
0.83	0.54642	2258	4.7596	.3115	0.30659	1072
0.84	0.56975	2333	4.4669	.2927	0.31797	1138
0.85	0.59352	2377	4.1914	.2755	0.33004	1207
0.86	0.61774	2422	4.9317	.2597	0.34293	1289
0.87	0.64237	2463	3.6865	.2452	0.35675	1382
0.88	0.66745	2508	3.4541	.2324	0.37160	1485
0.89	0.69297	2552	3.2333	.2208	0.38764	1604
0.90	0.71889	2592	3.0231	.2102	0.40508	1744
0.91	0.74523	2634	2.8226	.2005	0.42422	1914
0.92	0.77200	2677	2.6300	.1926	0.44528	2106
0.93	0.79913	2713	2.4450	.1850	0.46888	2360
0.94	0.82668	2755	2.2657	.1793	0.49552	2664
0.95	0.85461	2793	2.0966	.1751	0.52618	3066
0.96	0.88294	2833	1.9176	.1730	0.56225	3607
0.97	0.91164	2870	1.7426	.1740	0.60619	4394
0.98	0.94073	2909	1.5635	.1801	0.66203	5684
0.99	0.97018	2945	1.3627	.2008	0.74542	8239
1	1	2982	1	.3627	1	25458

Here it must be remarked that the values taken by the quantities  $\Pi$ ,  $W$ , and  $w$  at the critical temperature, at which  $\lambda=0$ , and which values may be denoted by  $\Pi_c$ ,  $W_c$ , and  $w_c$ , can be obtained from the expressions above mentioned, contained in § 3 of my previous paper, if the series contained in § 4 be also taken into account, as follows:—

$$\Pi_c = \frac{1}{8\gamma}; \quad W_c = 2\gamma; \quad w_c = 2\gamma. \quad . \quad . \quad . \quad (6)$$

These three values can hence be regarded as determined, just like the value  $\Theta_c$ , directly by the constant  $\gamma$ ; and accordingly the following fractions can be formed:—

$$\frac{\Pi}{\Pi_c}, \quad \frac{W}{W_c}, \quad \text{and} \quad \frac{w}{w_c}.$$

It is these fractions whose values are given in the Table (p. 133) by the side of the corresponding gradually increasing values of the fraction  $\Theta/\Theta_c$  denoted by  $\theta$ .

§ 2. In the foregoing Table is exhibited a relation, equally holding true for all substances, of the quantities  $\Pi$ ,  $W$ , and  $w$  to a temperature-function  $\Theta$  which is still left undetermined. Now what the form of the relation between those quantities and the *temperature itself* is, whether and in what degree it also agrees for different substances\*, depends on the behaviour of that temperature-function. In my investigation I started originally from the hypothesis that the temperature-function could be represented by an expression containing only one constant, dependent on the nature of the substance; but I found, on closer consideration, that a satisfactory accordance with experiment cannot be attained in so simple a manner. After various comparisons I obtained, as the most suitable form of an equation for the determination of the fraction which we have denoted by  $\Theta/\Theta_c$ , the following:—

$$\frac{\Theta}{\Theta_c} = \frac{a}{T^n} - b, \quad . \quad . \quad . \quad . \quad (7)$$

\* Two older propositions on this relation I have long since discussed (Pogg. Ann. lxxii. p. 273, 1851, and *Abhandlungensammlung*, i. p. 119, 1834). If, namely, the temperatures which with different liquids belong to equal vapour-tensions be called *corresponding* temperatures, then, according to Dalton, *the differences between corresponding temperatures are equal*. Groshans, on the other hand, has set up an equation (Pogg. Ann. lxxviii. p. 112, 1849) which, supposing that the temperatures be reckoned from  $-273^\circ$  C., expresses that for any two liquids *all corresponding temperatures are proportional*. Of these two propositions the second certainly does not deviate so far from experience as the first, but still it deviates too far for it to be possibly admitted as expressing an actual physical law.

in which  $a$ ,  $b$ , and  $n$  are constants which have different values for different substances.

The question now is, to determine these constants for each substance.

In the first place, in regard to carbonic acid, in the formula which I constructed specially for it\*, I have given the temperature-function  $\Theta$  a very simple form, namely that which is obtained from equation (7) by putting in it  $b=0$  and  $n=2$ , by which it is transformed into

$$\frac{\Theta^c}{\Theta} = \frac{a}{T^2},$$

for which we can also write

$$\Theta = T^2 \cdot \text{const.}$$

I added, however, at the time of publishing that formula that I had tried to adjust certain differences still existing between it and Andrews's observations, but had again desisted on account of the uncertainty of the results of those observations.

What I said at that time of the then existing results of observation still holds good. In particular it must be remarked that Andrews's observations refer only to temperatures above  $0^\circ$ , while the formula must remain valid also below  $0^\circ$  down to the freezing-point of carbonic acid,  $-57^\circ$ , and hence requires for the determination of its constants the observed values of a similar range of temperatures. Now we possess, it is true, a series of tensions of saturated carbonic-acid vapour, published by Regnault†, which extends to  $-25^\circ$ , although not to  $-50^\circ$ ; but in the experiments by means of which Regnault found those numbers considerable sources of error appear to have prevailed. The tensions cited by Regnault for temperatures above  $0^\circ$  deviate considerably from those observed by Andrews‡; and it is particularly surprising that Regnault professes to have observed the tensions of saturated vapour of carbonic acid up to temperatures above  $42^\circ$ , while after Andrews's experiments it is now established that from  $31^\circ$  upwards there is no saturated carbonic-acid vapour, because condensation no longer takes place.

Under these circumstances I think it advisable to retain provisionally my above-mentioned formula for carbonic acid, as an approximately correct one, and to defer undertaking the more exact determination of the constants till reliable data of observation shall be available also for temperatures below  $0^\circ$  down to the freezing-point of carbonic acid.

\* Clausius, Wied. Ann. ix. p. 337 (1880).

† Regnault, *Relation des Expériences*, &c. ii. p. 625 (1862).

‡ Andrews, Proc. Roy. Soc. xxiii. p. 516 (1875).

§ 3. A substance specially suited for the comparison of the theoretically determined with the observed vapour-tensions is ether. For this we possess the series of tensions determined by Regnault\*, extending from  $-20^{\circ}$  to  $120^{\circ}$ , of which the reliability cannot be questioned, and a series of tensions by Sajotschewsky†, which extends from  $100^{\circ}$  to the critical temperature  $190^{\circ}$ .

Of these observed tensions I have employed three for the determination of the constants occurring in equation (7), and found the following numbers:—

$$a=2665; \quad b=0.76786; \quad n=1.19233.$$

By employing these numbers, for every value of T the corresponding values of  $\Theta, \Theta_c$  can be calculated from (7); and then the value belonging to it of the fraction  $\Pi/\Pi_c$  can be taken from the Table. From this fraction, which can also be written  $P T_c/P_c T$ , the value of P is immediately obtained, since  $P_c$  and  $T_c$  are known. In this way I have calculated the tensions for a series of temperatures advancing by increments of  $20^{\circ}$  each, and arranged them in the following Table under the designation P calc. For comparison I have added, under P obs., the observed values—below  $100^{\circ}$  those observed by Regnault, above  $100^{\circ}$  those observed by Sajotschewsky, and for  $100^{\circ}$  and  $120^{\circ}$  the mean values taken from the data of both observers.

$t$	$-20^{\circ}$	$0^{\circ}$	$20^{\circ}$	$40^{\circ}$	$60^{\circ}$	$80^{\circ}$
P calc. ...	0.0381	0.2427	0.572	1.195	2.265	3.978
P obs.....	0.0907	0.2426	0.569	1.193	2.270	3.977
$\Delta$ .....	-0.0026	+0.0001	+0.003	+0.002	-0.005	+0.001

$t$	$100^{\circ}$	$120^{\circ}$	$140^{\circ}$	$160^{\circ}$	$180^{\circ}$	$190^{\circ}$
P calc. ...	6.557	10.27	15.41	22.33	31.41	36.90
P obs.....	6.549	10.28	15.42	22.34	31.90	36.90
$\Delta$ .....	+0.008	- 0.01	- 0.01	- 0.01	- 0.49	0

The accordance between the calculated and the observed tensions is seen to be almost complete. Only at  $180^{\circ}$  does a difference of inadmissible magnitude occur, which, in comparison with the rest of the differences, is very striking. This, however, is doubtless occasioned by an inaccuracy of the observation-value, as is most clearly to be inferred from the

\* Regnault, *Relation des Expériences*, &c. ii. p. 393.

† Sajotschewsky, *Beiblätter*, iii. p. 741 (1879).



fact that Sajotschewsky himself, by means of an empiric formula deduced from the rest of the observation-values, has determined the tension at  $180^\circ$  to be 31.56 instead of 31.90, whereby the difference from the value derived from our Table is reduced from 0.49 to 0.15.

The values of  $W/W_c$  and  $w/w_c$ , as well as those of  $\Pi/\Pi_c$ , are given in our Table.

In order to deduce the values of  $W$  and  $w$  from these fractions,  $W_c$  and  $w_c$  and consequently, according to (6), the constant  $\gamma$  must be known, for the determination of which the constant  $R$  is again requisite. The latter is obtained in the following manner:—The quantity  $R$  is, in accordance with its signification, inversely proportional to the specific gravities possessed by the substances in the perfectly gaseous state. Now the value of  $R$  for atmospheric air is known\*, namely 29.27; and from this follows for ether, if  $d$  denotes the specific gravity, referred to air, of the vapour of ether in the state of a perfect gas:—

$$R = \frac{29.27}{d}. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The question now is, which specific gravity is to be ascribed to ether vapour in the perfectly gaseous state? That, I believe, can be admitted as such, which is obtained when, in accordance with the accepted chemical formula for ether, it is assumed that 1 vol. oxygen and 10 vols. hydrogen, with the corresponding quantity of carbon, give 2 vols. ether vapour, namely the sp. gr. 2.5604. On employing this number for  $d$ , the preceding equation gives

$$R = 11.4318.$$

This value refers to 1 kilogram of the substance considered, and therefore, in the present case, of ether; and in it the unit of volume is 1 cubic metre, and the unit pressure the pressure exerted by a weight of 1 kilogram spread over a surface of 1 square metre. These units we will retain in the determination of the other constants and the quantities  $s$  and  $\sigma$ .

To determine  $\gamma$ , according to (6) we can put

$$\gamma = \frac{1}{8\Pi_c} = \frac{RT_c}{8P_c}; \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and from this, if, employing the values found by Sajotschewsky for the critical temperature and pressure, we put

$$T_c = 273 + 190 = 463 \quad \text{and} \quad P_c = 36.9 \times 10333,$$

\* See Clausius, *Mechanische Wärmetheorie*, i. p. 55.

and for R the previously determined value, we get

$$\gamma = 0.0017352.$$

Now, when with the help of the value of  $W_c$  and  $w_c$  represented by  $2\gamma$  the quantities  $W$  and  $w$  have been obtained from the above-mentioned fractions  $W/W_c$  and  $w/w_c$  and we wish from those quantities to arrive at the volumes  $s$  and  $\sigma$  of the ether vapour and liquid, we must for that purpose know the constant  $\alpha$  also, since  $s = W + \alpha$ , and  $\sigma = w + \alpha$ . For the determination of  $\alpha$  it is best to employ any observed volume of the liquid, from which the calculated value of  $w$  for the same temperature is to be subtracted. At  $0^\circ$ , according to Kopp, liquid ether has the specific gravity 0.73658, from which, considering that the volume  $\sigma$  refers not to the pressure of 1 atm., but to that of 0.2426 atm., we get  $\sigma = 0.0013578$ . In like manner we get for  $20^\circ$ , according to Kopp,  $\sigma = 0.0014001$ . If with the help of these quantities we determine  $\alpha$  and take the mean of two closely accordant values, we find

$$\alpha = 0.0010876.$$

It may here at once be added, further, that after the determination of  $\gamma$  and  $\alpha$  the value of  $\beta$  also immediately results, since  $\beta = \gamma - \alpha$ . There comes, namely,

$$\beta = 0.0006476.$$

Employing the found values of the constants, we can now calculate from the fractions  $W/W_c$  and  $w/w_c$  the quantities  $s$  and  $\sigma$ , and obtain for the above-considered series of temperatures the following values:—

$t$	$-20^\circ$	$0^\circ$	$20^\circ$	$40^\circ$	$60^\circ$	$80^\circ$
$s \dots$	3.182	1.238	0.5562	0.2793	0.1524	0.08883
$\sigma \dots$	0.001318	0.001356	0.001402	0.001455	0.001520	0.001600

$t$	$100^\circ$	$120^\circ$	$140^\circ$	$160^\circ$	$180^\circ$	$190^\circ$
$s \dots$	0.05417	0.03408	0.02175	0.01373	0.008016	0.004558
$\sigma \dots$	0.001702	0.001837	0.002030	0.002335	0.002982	0.004558

In conclusion, the form which the general equation (3) assumes after the determination of  $\Theta$  may now be added. According to (7) and (4) we must put

$$\frac{1}{\Theta} = \frac{1}{\Theta_c} (aT^{-n} - b) = \frac{27\gamma}{8} (aT^{-n} - b).$$

For this, by introducing new constants, we can write more briefly

$$\frac{1}{\Theta} = AT^{-n} - B; \dots \dots \dots (10)$$

and thereby (3) is transformed into

$$\frac{p}{RT} = \frac{1}{v-a} - \frac{AT^{-n}-B}{(v+\beta)^2} \dots \dots \dots (11)$$

The values of the constants A and B for ether are obtained from the above-given values of  $a$ ,  $b$ , and  $\gamma$  as follows:—

$$A=15.607; \quad B=0.0044968.$$

§ 4. The substances in which it has not yet been possible to extend the observations of the vapour-tensions up to the critical temperature, present difficulties, in the determination of the constants  $a$ ,  $b$ , and  $n$  in equation (7), which are the greater the more distant the highest observed temperature still is from the critical temperature. If, namely, that distance is very great, the alterations of the constants which, in the temperature-interval for which observations are available, occasion but slight differences in the calculated vapour-densities, yet have for their result a considerable difference in the calculated critical temperature and the pressure corresponding to it.

To these substances belongs *water*. I have tried, from Regnault's observations of tensions, which extend to somewhat above  $220^{\circ}$ , to deduce the most probable values of the constants, and, after various comparisons, have arrived at the following numbers:—

$$a=5210; \quad b=0.85; \quad n=1.24.$$

With the aid of these numbers, and on the supposition that for the temperature of  $100^{\circ}$  the vapour-tension amounts to 1 atmosphere, I have, as in the case of ether, deduced the vapour-tensions for a series of temperatures advancing by increments of  $20^{\circ}$  each, and found the following values. So far as the observation-values extend, I have added them also, for comparison, selecting those values which Regnault took direct from the curves constructed by him, and which he regarded as the most immediate result of his observations. Where he gives two values, obtained from different curves, I have taken their mean. Beneath the observed tensions are placed the differences from the calculated ones; and I have moreover given in this Table the calculated values of  $s$ , which will be spoken of further on.

$t$	0°	20°	40°	60°	80°	100°
P calc....	0.00574	0.02248	0.07183	0.1956	0.4665	1
P obs. ...	0.00605	0.02288	0.07225	0.1958	0.4666	1
$\Delta$ .....	0.00031	0.00040	0.00042	0.0002	0.0001	0
$s$ .....	216.6	59.30	19.81	7.725	3.422	1.677
$t$	120°	140°	160°	180°	200°	220°
P calc....	1.962	3.571	6.106	9.907	15.37	22.97
P obs. ...	1.960	3.569	6.118	9.922	15.35	22.88
$\Delta$ .....	-0.002	-0.002	0.012	0.015	-0.02	-0.09
$s$ .....	0.8927	0.5085	0.3060	0.1924	0.1253	0.08371
$t$	240°	260°	280°	300°	320°	332°·32
P calc....	33.23	46.73	64.15	86.27	113.9	134.1
$s$ .....	0.05700	0.03912	0.02680	0.01796	0.01111	0.005892

Comparison of the calculated and observed tensions shows a very satisfactory accordance within the entire interval from 0° to 220°; accordingly it may well be assumed as probable that the calculated values of the tensions for the higher temperatures also, as well as the calculated critical temperature 332°·32, and the corresponding pressure of 134 atmospheres, do not deviate too far from the truth.

Now, as to the other constants which occur in the formulæ, for  $R$ , according to equation (8), if we put therein for  $d$  the value 0.6221, which results from the values found by Regnault for the specific gravities of hydrogen and oxygen, we get

$$R = 47.05.$$

From this it follows, further, according to (9), if for  $T_c$  and  $P_c$  the values above found be employed, that

$$\gamma = 0.002569.$$

To determine  $\alpha$ , from an observed volume of liquid water the calculated value of  $w$  for the same temperature must be subtracted. Now liquid water, when heated from 0°, exhibits the peculiar phenomenon that at first it contracts, and only expands above 4°, and that even then, within a considerable interval of temperature, its coefficient of expansion is much more variable than those of other liquids. This phenomenon, which is unquestionably connected with those molecular forces

which at the freezing of water act as forces of crystallization, is not expressed in our equation employed for the determination of  $w$ , because in constructing that equation forces of this kind are not taken into consideration. Hence arises for the determination of  $\alpha$  an uncertainty, since different values of  $\alpha$  are obtained, according to the temperature to which the water-volume employed for the determination refers. If the observed volume at  $20^{\circ}$  is employed, there comes

$$\alpha = 0.000754;$$

and when this number is subtracted from that above given for  $\gamma$ , we get

$$\beta = 0.001815.$$

Upon the calculated values of the vapour-volume  $s$  the uncertainty existing in relation to the constant  $\alpha$  has only a very slight influence, since the total quantity of  $\alpha$ , in comparison with the vapour-volume at all temperatures which are not too near the critical temperature, is very small. The calculated values of  $s$  for the above-considered series of temperatures are, as already mentioned, annexed to the last Table; they exhibit the volume, in cubic metres, of a kilogram of vapour.

If, lastly, to the equation determining the pressure  $p$  be given the form adduced under (11),

$$\frac{p}{RT} = \frac{1}{v - \alpha} - \frac{AT^{-n} - B}{(v + \beta)^2},$$

the constants  $A$  and  $B$  herein occurring have for water the following values:—

$$A = 45.17; \quad B = 0.00737.$$

## XVI. *Proceedings of Learned Societies.*

### GEOLOGICAL SOCIETY.

[Continued from p. 71.]

December 7, 1881.—Robert Etheridge, Esq., F.R.S., President, in the Chair.

THE following communications were read:—

1. "The Zones of the Blackdown Beds and their Correlation with those at Haldon, with a List of the Fossils." By the Rev. W. Downes, B.A., F.G.S.

The author, after some remarks on the inexact way in which



fossils had been collected from or referred to the Blackdown beds, and a sketch of the literature of the subject, passed on to a correlation of the Blackdown beds with deposits in other localities. He pointed out that they do not contain a sufficient number of species in common with the Marne de Bracquagnies to justify an identification with this. He compared them with the Haldon beds, and, by a comparison of the fossils bed by bed, showed that of 196 Blackdown species (omitting a few corals) 50 occur at Haldon; the latter section, however, represents not the whole, but only the upper part of the former, nine beds in the lower part of it being without representatives at Haldon. Here also the higher beds contain a thin band distinguished by a distinct and all but unique fauna (the zone containing the corals described by Prof. Duncan). Comparing the Blackdown beds with lists of Cretaceous fossils from other localities, it would appear that we have neither exclusively Upper-Greensand forms at the top, nor exclusively Lower-Greensand forms at the bottom, nor exclusively Gault forms in the middle.

2. "On some new or little-known Jurassic Crinoids." By P. Herbert Carpenter, Esq., M.A.

3. "Notes on the Polyzoa of the Wenlock Shales, Wenlock Limestone, and Shales over the Wenlock Limestone. From material supplied by G. Maw, Esq., F.L.S., F.G.S." By G. R. Vine, Esq.

December 21.—Robert Etheridge, Esq., F.R.S., President,  
in the Chair.

The following communications were read:—

1. "The Torridon Sandstone in relation to the Ordovician Rocks of the Northern Highlands." By C. Callaway, Esq., M.A., D.Sc., F.G.S.

The author pointed out that the apparent difference in dip between the Torridon sandstone and the overlying quartzite in the neighbourhood of Loch Broom was due to some markings in the former which suggested a direction of bedding which was not the real one, and that the one rock passed gradually into the other. The two are perfectly conformable at Strath Auchall, where the junction can be well studied, also between Unaport and Strath Kennort, on the north side of Loch Assynt and south of Unaport. The author then considers that there is proof of the conformity of the quartzites with the Torridon sandstone, and that there is no unconformity as generally suggested. In this case it appears to him to follow that the Torridon sandstone must be either Ordovician or Upper Cambrian in age, and that the former is more probable, as the overlying quartzite is not more than some 500 feet thick, so that the united thickness of the two hardly exceeds at most that of the Arenigs of Shropshire or South Wales.

2. "The Precambrian (Archæan) Rocks of Shropshire." Part II. By C. Callaway, Esq., D.Sc., F.G.S.

The author described the western axis of Archæan rocks in

Shropshire, which runs roughly parallel with the Wrekin and Caradoc ranges at a distance of from 6 to 7 miles, the intervening district being chiefly occupied by the Longmynd rocks. They are exposed over a line about 11 miles long, forming usually low hills or ridges trending S.S.W. Pontsford Hill, however, at the northern end, projects prominently into the Shropshire plain. In the lower part of this hill are purple rhyolites banded and spherulitic, the latter structure being exhibited in chalcedony filling cavities of the rock. Compact dolerite forms the upper part of the hill. At Lyd's Hole a junction of the Cambrian Grits with the underlying rhyolites is seen. Conglomerates containing the latter rock also occur. At Gatten Lodge are purple hornstones; at Knoll's Ridge somewhat similar rocks, with others that appear intrusive; at Cold Hill purple hornstone and breccia; and at Chissol a greenish hornstone. The rocks of Knolls Wood are probably about on the horizon of those of Caer Caradoc, grits perhaps derived from a gneissic area. Stratigraphical as well as lithological considerations lead the author to the opinion that the series is Precambrian.

3. "The Red Sands of the Arabian Desert." By J. A. Phillips, Esq., F.R.S., F.G.S.

The author described the general characters of the Nefūd, or great red desert of Northern Arabia, which consists of a series of parallel ridges of considerable elevation, no doubt at some period piled up by the action of strong winds, but now no longer undergoing much change of position, as is evidenced by the fact that sticks and stones remain for many days uncovered on the surface, and that the landmarks made use of in crossing the desert appear to be permanent. A specimen of the sand of this desert received by the author from Lady Anne Blunt, is composed of well-rounded red grains from  $\frac{1}{50}$  to  $\frac{1}{30}$  inch in their longest diameter, which are rendered colourless by treatment with hydrochloric acid, the material thus removed amounting to .21 per cent., or a little more than  $\frac{1}{500}$  of the total weight operated upon, and consisting of ferric oxide with a small quantity of alumina. The sand dried after the action of hydrochloric acid gave on analysis:—

Silica .....	98.53
Protoxide of iron .....	0.28
Alumina .....	0.88
Lime, magnesia, and alkalies .....	trace.
	<hr/>
	99.69

The external coating of ferric oxide must therefore have been deposited subsequently to the rounding of the grains; it could not have been derived from an external decomposition of the grains themselves; and it becomes difficult to imagine in what manner the superficial red coating can have been produced. The author compared these grains with those of the millet-seed sandstones of

Triassic age, with which they closely agree in character, but remarked that the conditions of their occurrence were apparently quite different.

4. "Analyses of five Rocks from the Charnwood-Forest District." By E. E. Berry, Esq. Communicated, with Notes, by Prof. T. G. Bonney, F.R.S., Sec. G.S.

These analyses are of hornblendic granite from Mount Sorrel, "syenite" from Markfield, Garendon, and Croft Hill, and "porphyroid" from Sharpley. In the main they confirm the views expressed by Messrs. Hill and Bonney in their communications on the subject, arrived at from microscopic examination, as to the nature and affinities of these rocks.

January 11, 1882.—R. Etheridge, Esq., F.R.S., President,  
in the Chair.

The following communications were read:—

1. "On the Chalk Masses or Boulders included in the Contorted Drift of Cromer, their Origin and Mode of Transport." By T. Mellard Reade, Esq., F.G.S.

The author referred to the occurrence in the Contorted Drift of Cromer of large masses of chalk, and came to the following conclusions:—The travelled masses are derived from sea-cliffs and the result of landslips, aided by the penetration of water forming ice, intrusive in fissures which detached them from the parent rocks. Water rising from subterranean sources accumulated as ice around the fallen masses, and was then frozen into the shore-ice. Ice-floes brought into contact with these masses were also frozen into them, forming a raft capable of floating away the boulders. The incline of the shore and the rise and fall of the tides on the breaking-up of the ice would suffice to launch the rafts into the sea; and they probably floated in water not more than 200 feet deep. The frequency of these boulders and their accumulation in the Cromer deposit point to their having been arrested by the shoaling of the water and by stranding on a submarine bank. The nature of the chalk showed that they had not travelled far.

2. "Observations on the two Types of Cambrian Beds of the British Isles (the Caledonian and Hiberno-Cambrian), and the Conditions under which they were respectively deposited." By Prof. Edward Hull, LL.D., F.R.S., F.G.S.

In this paper the author pointed out the distinctions in mineral character between the Cambrian beds of the North-west Highlands of Scotland and their assumed representatives in the east of Ireland and in North Wales. In the former case, which included the beds belonging to the "Caledonian type," the formation consists of red or purple sandstones and conglomerates; in the latter, which included the beds belonging to the "Hiberno-Cambrian type," the formation

consists of hard green and purple grits and slates contrasting strongly with the former in structure and appearance.

These differences the author considered were due to deposition in distinct basins lying on either side of an Archæan ridge of crystalline rocks which ranged probably from Scandinavia through the central highlands of Scotland, and included the north and west of Ireland, with the counties of Donegal, Derry, Mayo, Sligo, and Galway—in all of which the Cambrian beds were absent, so that the Lower Silurians repose directly and unconformably on the crystalline rocks of Laurentian age.

As additional evidence of the existence of this old ridge, the author showed that when the Lower Silurian beds were in course of formation, the Archæan floor along the west of Scotland must have sloped upwards towards the east; but he agreed with Professor Ramsay that the crystalline rocks of the Outer Hebrides formed the western limit of the Cambrian area of deposition, and that the basin was in the form of an inland lake.

On the other hand, looking at the fossil evidence both of the Irish and Welsh Cambrian beds, he was of opinion that the beds of this basin were in the main, if not altogether, of marine origin, and that the basin itself had a greatly wider range eastward and southward, the old Archæan ridge of the British Isles forming but a small portion of the original margin.

### 3. "The Devon-Silurian Formation." By Prof. E. Hull, LL.D., F.R.S., F.G.S.

The beds which the author proposed to group under the above designation are found at various parts of the British Isles, and to a slight extent on the continent. The formation, however, is eminently British, and occurs under various local names, of which the following are the principal :—

#### ENGLAND AND WALES.

*Devonshire.*—The Foreland Grits and Slates lying below the Lower Devonian beds ("Lynton Beds").

*Welsh Borders.*—"The passage-beds" of Murchison, above the Upper Ludlow Bone-bed, and including the Downton Sandstone, and rocks of the Ridge of the Trichrug. These beds form the connecting link between the Estuarine Devonian beds of Hereford (generally, but erroneously, called the "Old Red Sandstone") and the Upper Silurian Series.

*South-east of England* (Sub-Cretaceous district).—The author assumed, from the borings at Ware, Turnford, and Tottenham Court Road described by Mr. Etheridge, that the Devon-Silurian beds lie concealed between Turnford and Tottenham Court Road on the south and Hertford on the north.

#### IRELAND.

*South.*—"The Dingle Beds," or "Glengarriff Grits and Slates,"

lying conformably on the Upper Silurian Beds, as seen in the coast of the Dingle promontory and overlain unconformably by either Old Red Sandstone or Lower Carboniferous beds, 10,000 to 12,000 feet.

*North.*—"The Fintona Beds," occupying large tracts of Londonderry, Monaghan, and Tyrone, resting unconformably on the Lower Silurian beds of Pomeroy, and overlain unconformably by the Old Red Sandstone or Lower Carboniferous beds, 5000 to 6000 feet in thickness.

SCOTLAND.

Beds of the so-called "Lower Old Red Sandstone," with fish and crustaceans, included in Professor Geikie's "Lake Orcadie, Lake Caledonia, and Lake Cheviot," underlying unconformably the Old Red Sandstone and Lower Calciferous Sandstone, and resting unconformably on older crystalline rocks. Thickness in Caithness about 16,200 feet.

The author considered that all these beds were representative of one another in time, deposited under lacustrine or estuarine conditions, and, as their name indicated, forming a great group intermediate between the Silurian on the one hand and the Devonian on the other. He also submitted that their importance, as indicated by their great development in Ireland and Scotland, entitled them to a distinctive name such as that proposed.

XVII. *Intelligence and Miscellaneous Articles.*

ON THE LUMINOUS INTENSITIES OF THE RADIATIONS EMITTED BY INCANDESCENT PLATINUM. BY PROF. J. VIOLE.

**I** HAVE measured at different temperatures, and for various radiations, the light-intensities of incandescent platinum.

I have selected as temperatures some of the melting-points which I previously determined in degrees of the air-thermometer, and which I here repeat (correcting the melting-point of gold, which was set down by mistake at 1035°):—

Melting-point of silver	.....	954
" "	gold	..... 1045
" "	palladium	..... 1500
" "	platinum	..... 1775

In order to get some platinum, for example, at 1045°, a button of platinum of about 200 grams weight was put into a crucible of unglazed porcelain, which was introduced into a second crucible, made of fireclay, and already containing at its lower part 500 grams of gold. The whole was placed in a large vertical Perrot furnace traversed along its axis by a long fireclay tube, through which the surface of the platinum could be seen. It was heated up to the fusion of the gold; the arrival gas-cock was then, to a slight extent,



partially closed, so as to induce a commencement of solidification; the cock was again touched; and by thus modifying the arrival of the gas, it was kept, without too much difficulty, just at the point of fusion. The great mass of the furnace secures a sufficiently extensive constant thermal field, and permits its constancy to be easily maintained.

The operation was precisely the same for bringing the platinum to and keeping it at  $954^{\circ}$ , the outer crucible containing silver instead of gold.

It is rather more difficult to accomplish the operation in the palladium bath; it can, however, be done by feeding the furnace with a Schlœsing blowpipe and protecting the crucibles by graphite casings. Palladium can also be made use of more simply, even at its melting-point, by employing Deville and Debray's furnace and blowpipe.

For the photometric measurements I employed successively the two methods by which luminous intensities are usually measured—the comparison of two contiguous luminous fields, and the extinction of the isochromatic lines called forth by a sensitive polariscope. I used for this purpose the Gouy spectrophotometer and a Trannin spectrophotometer, suitably modified for the present use; and although each of these apparatus suits better than the other in certain cases, I thus obtained a valuable control of the results. The source taken as the term of comparison, in all the experiments, was the Carcel standard lamp burning 42 grams of oil per hour.

The following Table contains the results thus obtained, plus those of a series made at  $775^{\circ}$  (temperature measured by the calorimetric method).

Temperatures.	Intensities.			
	$\lambda=656.$	$\lambda=589.2.$	$\lambda=535.$	$\lambda=482.$
	C.	D.	(E=527)	(F=486)
$775^{\circ}$ .....	0.00300	0.00060	0.00030	
$954^{\circ}$ .....	0.01544	2.01105	0.00715 (?)	
$1045^{\circ}$ .....	0.0505	0.0402	0.0265	0.0162
$1500^{\circ}$ .....	2.371	2.417	2.198	1.894
$1775^{\circ}$ .....	7.829	8.932	9.759	12.16

If, then, the luminous intensity of incandescent platinum at  $954^{\circ}$ ,  $1045^{\circ}$ , and  $1500^{\circ}$ , in the various simple radiations, be successively taken for the unit, we get for the relative intensities:—

$775^{\circ}$ ...	0.19	...	...	0.05	...	...	0.04						
$954^{\circ}$ ...	1	...	...	1	...	...	1						
$1045^{\circ}$ ...	3.27	1	...	3.64	1	...	3.71	1	...	1			
$1500^{\circ}$ ...	154	47	1	219	60	1	307	83	1	117	1		
$1775^{\circ}$ ...	507	155	3.30	809	222	3.70	1365	368	4.44	752	6.42		

Various consequences follow from these numbers, both for the

law of radiation at high temperatures, and in regard to the measurement of those high temperatures by photometry. I shall shortly resume these two important questions, at present confining myself to indicating the formula

$$I = mT^3(1 + \epsilon\alpha^{-T})^T$$

as well representing the results.  $I$  is the intensity of a simple radiation;  $T$ , the absolute temperature;  $m$ ,  $\epsilon$ , and  $\alpha$ , constants which will have to be determined.—*Comptes Rendus de l'Académie des Sciences*, t. xcii. p. 866 (1881).

#### AN APPLICATION OF ACCIDENTAL IMAGES. (SECOND NOTE.)

BY J. PLATEAU.

In my first Note\* I showed that the distance to which we refer the moon in the sky can be pretty exactly estimated by projecting upon a wall the dark accidental image which succeeds the contemplation of the moon itself, then receding from or approaching towards the wall till the diameter of the image is judged to be equal to that of the celestial object, and, lastly, measuring the distance at which the observer is from the wall when this condition appears to be fulfilled. I said then that one of my sons had by this means obtained about 51 metres for the distance in question. As this value seemed very small, I have more recently induced my son to make a control experiment, although with less precision: he sought a position, in front of the wall, such that the diameter of the dark image appeared to him as exactly as possible half of that of the moon; and this required him to be distant from the wall not more than 23·5 metres. Now, in virtue of the known proportionality between the diameter of the accidental image and the distance to which it is projected, double the above quantity, viz. 47 metres, consequently represented approximately the distance at which my son instinctively placed the moon; and it will be seen that this latter distance, though not coinciding with the 51 metres of the previous experiment less subject to error, is nevertheless of the same order.

M. l'abbé Thirion, Professor at the Collège de la Paix at Namur, has since published† an estimate at which he arrived by a quite different procedure. He assembled twelve of his pupils, and asked each of them to trace on a black board a circumference of the size he saw the moon in the sky. These twelve circumferences were very unequal; the smallest was only 19 centim. in diameter, while

\* *Bull. Acad. Roy. Belg.* [2] xlix. 1880, p. 316; *Phil. Mag.* August 1880, p. 134.

† *La Lune—les préjugés et les illusions*: Bruxelles, 1881.

*Phil. Mag.* S. 5. Vol. 13. No. 79. Feb. 1882.

the largest was 72: the mean of the twelve was 32 centimetres. Starting from this, and from the mean value 31' of the angle subtended by the moon's diameter, M. Thirion finds about 35 metres for the distance sought—that is to say, for the mean of those to which his pupils respectively referred our satellite.

Lastly, Dr. Charpentier\*, who wanted, for the discussion of an entoptic phenomenon, to know to what distance his eye “projects the retinal images in the vision of remote objects,” determined accessorially, by again a different procedure, that at which he places the moon. That heavenly body appears to him to have a diameter of only 15 centim., and to present the same breadth as a disk of 7·5 millim. diameter held at 645 millim. from the eye. From this he deduces, for the apparent distance of the moon, the value 12·9 metres.

From all this it follows, in the first place, that the distance in question varies considerably from one observer to another, and, in the second place, that it is always much less than would *a priori* have been believed.

I have applied my accidental-image process to the investigation of an element for the approximate determination of which I believe it is the only one practicable. When in the daytime and in calm weather we look at the sky, it presents to us the appearance of an azure surface in the form of an elliptical vault; but at what distance do we picture to ourselves this imaginary surface? Our eyes then dive into an indefinite medium; and yet they stop somewhere; but where? To what distance do they adapt themselves? It is this, again, that the accidental images will permit us to appreciate. As I said before, I reside in a house situated in a square, and with its frontage facing the south. The experiment was made as follows:—In July last, about 4 P. M., the weather being calm, a square of white paper marked with a black point in the centre was placed upon a black surface: and the whole was put on the sill of an open window. My son-in-law contemplated for 20 seconds the white square, keeping his eyes fixed on the black point; he then gazed at the sky, at a sufficient height above the opposite houses of the square, in order to observe the dark accidental image, after which he projected this upon the wall of one of those houses, and found that it had increased a little in magnitude: the respective sides of the image in the two conditions were, in his estimation, in the ratio of 5 to 6. My son Felix performed the same operations; and for him the ratio was about 4 to 5. The two observers were at 36 metres from the houses opposite; consequently it follows, from the proportionality above mentioned, that my son-in-law referred the celestial vault to the distance of 30 metres approximately, and my son to that of 29 metres. Therefore it is an equally inconsiderable distance that is attributed to the vault of heaven.

\* “Illumination violette de la rétine sous l'influence d'oscillations lumineuses,” *Comptes Rendus*, t. xcii. 1881, p 355.

I asked myself if the greater or less brightness of the sky has not an influence upon the distance sought. To ascertain this I requested my son-in-law to repeat the experiment at night, illuminating the white square by means of a lamp. He did so in the middle of September, at 9 in the evening, the sky being calm and without moon. To remove all lateral light, an assistant took away the lamp as soon as the observer, after contemplating the white square, directed his eyes to the sky. Now, to my great surprise, the result was sensibly the same as in the day experiment. Afterwards my second son operated, and found a value still of the same order. So the brightness appears to have no notable influence upon the appreciation of the distance at which the point observed in the celestial vault is instinctively placed.—*Bulletins de l'Académie Royale de Belgique*, sér. 3, tome ii. nos. 9 and 10, Sept. and Oct. 1881.

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ON SOME CONSEQUENCES OF GAUSS'S PRINCIPLE IN ELECTRO-STATICS. BY M. CROULLEBOIS.

M. Bertrand\* has deduced from Gauss's principle several important theorems relative to electrostatics; following the same path, I have obtained some interesting relations, and particularly the simplified demonstration of Clerk Maxwell's theorem.

I. Gauss's proposition  $\Sigma MV' = \Sigma M'V$  is a pure identity if the potentials be replaced by the expressions which the definition furnishes. This relation can be arrived at independently of any analytical form attributed to the function  $V$ , by resting on the notion of electric energy. Let us consider a conductor of charge  $M$ , at the potential  $V$ , the potential energy of which is  $\frac{MV}{2}$ ; let us vary the charge from  $M$  to  $M'$ , the potential will vary from  $V$  to  $V'$ , and the increase of energy, equal to the electrical work expended to bring the additional charge  $M' - M$  from infinite distance to the conductor, will be

$$(M' - M) \frac{V + V'}{2}.$$

We shall therefore have for the final energy,

$$M'V' = MV + (M' - M)(V + V'),$$

from which, after simplification, and for a system of conductors,

$$\Sigma MV' = \Sigma M'V. \dots\dots\dots (1)$$

II. From the two sides of the equality (1) let us subtract  $MV$  and put  $M' - M = \mu$  and  $V' - V = u$ , we shall have

$$\Sigma Mu = \Sigma V\mu, \dots\dots\dots (2)$$

\* *Journal de Physique*, t. iii. p. 74.

or, if the simultaneous modification of the charges and potentials is infinitesimal,

$$\Sigma M \delta V = \Sigma V \delta M. \dots\dots\dots (2')$$

whence this theorem, a consequence of Gauss's principle explained according to § I. :—

*In a system of fixed conductors, in which two distinct systems of equilibrium are considered, the sum of the products of the initial charge of each conductor and the variation of its potential from one state to the other is equal to the sum of the products of the initial potential and the variation of the charge.*

III. When conductors, maintained at constant potentials, are left to their mutual actions, the energy of the system tends towards a maximum.

Clerk Maxwell has demonstrated this theorem\* by means of the linear equations which exist between the potentials and the charges. The following process is more direct and speedy.

Let us suppose, at the beginning, each conductor  $A_1, A_2, \dots$  insulated, and impress on the system an *infinitely small deformation*: the charges  $M_1, M_2, \dots$  do not change; there are for the respective potentials the falls  $\delta V_1, \delta V_2, \dots$ ; the loss of energy, *equal to the external work accomplished*, is

$$\delta W = -\frac{1}{2} \Sigma M \delta V.$$

Now, the conductors being fixed, let us connect them to constant batteries, in order to restore the potentials to their original values. This restoration of the potentials cannot be effected without additional charges  $\delta M_1, \delta M_2, \dots$ , regulated by the relation (2'). The *positive* variation of the initial energy will therefore be

$$\delta' W = +\frac{1}{2} \Sigma M \delta V.$$

We hence conclude that

$$\delta W + \delta' W = 0,$$

and

$$\delta' W - \delta W = \Sigma M \delta V.$$

Therefore (1) the work accomplished, during the displacement, by the electrical forces is equal to the augmentation of energy of the system; (2) the energy furnished by the sources is equal to twice one or the other of those quantities, and is expended *exactly*, half in mechanical work, half in electrical work or potential energy.

According to the equality (2), the preceding theorem applies to a *finite deformation*; but, for its application to the theory of electrometers, there is, as is known, only occasion to consider an elementary modification.—*Comptes Rendus de l'Académie des Sciences*, Jan. 9, 1882, t. xciv. pp. 74–76.

\* 'Electricity and Magnetism,' vol. i. p. 96.



THE  
LONDON, EDINBURGH, AND DUBLIN  
PHILOSOPHICAL MAGAZINE  
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[FIFTH SERIES.]

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MARCH 1882.

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XVIII. *Electro-optic Experiments on various Liquids.* By  
JOHN KERR, LL.D., *Free Church Training College, Glasgow*\*.

THE following notes of experiments are intended as a sequel to two of my former papers on Electro-optics, which appeared in the *Philosophical Magazine* for August and September 1879. In those papers I gave an account of methods and results in connexion with twenty-seven liquid dielectrics; thirteen of them belonging to the class of fixed oils, and all clearly active as nonconductors, with the one exception of nitrobenzol. Shortly afterwards, Professor Röntgen repeated and varied my experiments, and produced a very interesting investigation on the subject; and, in particular, he extended the list of electro-optically active dielectrics by the important addition of three bodies—water, sulphuric ether, and glycerine†. To the list already published I have now to add more than a hundred new liquids, with specification of their actions as positive or negative, strong or weak, pure or impure. I shall give first a condensed account of the experiments, and then a summary of results (art. 29).

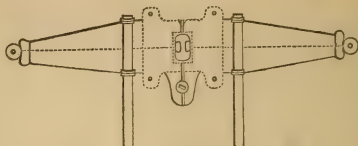
*Apparatus and Methods.*

1. The small plate cell is the principal instrument used in the present experiments. As I gave a full description of this

\* Communicated by the Author.

† There is a good account of Professor Röntgen's paper in Mr. Gordon's *Treatise on Electricity*.

important piece in the first of my two papers already referred to, I think that here I need only reproduce the diagram.



*Optical Arrangements.*—The plate cell, charged nearly full with the dielectric liquid, is stationed between the polarizing and analyzing Nicols, the faces of the liquid plate being always perpendicular to the line of vision. In most cases, the object viewed in the polariscope is a narrow and sharply-outlined flame, a flat and thin paraffin-flame presented edgewise, and seen exactly through the centre of the electric field. The first Nicol is fixed with its principal section at  $45^\circ$  to the horizon, or to the lines of force; and the second Nicol is fixed at extinction. When the light is well restored by electric force, the character of the effect as positive or negative is generally detected at a glance, and with perfect certainty, by the use of the hand-compensator. This is a small rectangular slip of thin plate glass, held in the observer's hands between the two Nicols, and simply stretched or compressed in a direction parallel to the lines of force.

*Electric Arrangements.*—These vary with circumstances, and are sometimes all employed successively in the examination of one dielectric. The liquid may be tried (1) as a nonconductor, (2) as a conductor, but without the jar, (3) with the jar, (4) with intense discharges of a Ruhmkorff's coil.

Every new liquid is tested for insulation in the first place. The outer balls of the cell are connected respectively with prime conductor and earth by unbroken wires, and the machine is set in motion. The test consists in bringing up the knuckle or an earth-connected ball to contact with prime conductor, and *receiving*, or *not receiving*, a spark.

(1) To try a liquid electro-optically as a nonconductor. The cell is placed in the polariscope at extinction, its outer balls being connected with prime conductor and earth by unbroken wires; the machine is set in motion, and the polariscope is watched for a restoration of the light from extinction. When there is a clear effect, it is tested by the hand-compensator, and characterized as positive or negative. This method has given distinct results with every moderately good insulator yet examined.

(2) When the prime conductor gives no sensible spark in the test for insulation, the first method fails, and the liquid is then tried as a conductor, but first without the jar. The wire from prime conductor to cell is broken, and the ends are inserted in two metallic balls, which are supported on insulating pillars, and separated by an air-interval. The machine being set in motion, the two balls are put in contact at every turn or half turn of the plate, so as to discharge the prime conductor through cell to earth; and the polariscope is watched for restoration at the instants of discharge. When the optical effect is moderately strong and not very abrupt, the hand-compensator works as well here as in the former case. There are many liquids (nitrobenzol, benzonitrile, amyl alcohol, &c.) which give intense restorations purely positive or purely negative when tried in this way, though they give no sure trace of effect when tried as nonconductors.

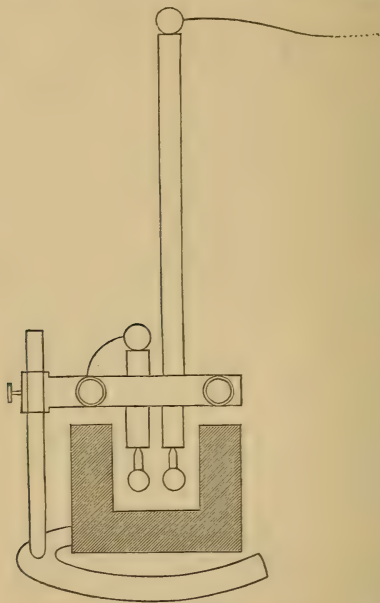
(3) When this method fails, the power is increased by the addition of a Leyden jar, whose knob and outer coating are connected respectively with prime conductor and earth. The machine is set in motion, and the discharging balls are brought into contact, first at every turn of the plate, then at every second turn, and so forward, till the optical effect is brought out with sufficient intensity. There are many liquids (butyl and propyl alcohols, propionic and acetic acids, &c.) which give pure and strong restorations at and above some point of this process, but no trace of effect without the jar.

(4) When these methods fail, the Winter's plate machine is abandoned, and a Ruhmkorff's coil is applied. The coil is worked by six large Grove's elements in series, and gives a powerful spark (8 to 10 inches in air). The cell is sometimes inserted in the circuit of the secondary coil by unbroken wires; in other cases, there are air-intervals left at the outer ends of the cell, which are traversed by spark discharges. It is found to be generally advisable, and sometimes necessary, to dispense with the automatic rheotome, and to work the instrument by hand, so as to obtain separate discharges at intervals of one or more seconds. With all precautions, the discharges are often too strong for perfect purity of electro-optic action, producing large disturbances in the liquid, and giving rise in a little time to intense heat-effects. There are several liquids (ethyl alcohol, distilled water, &c.) which have given good results by this method only.

2. *The Fusion-cell*, a small instrument similar to the plate cell, but adapted to higher temperatures, is represented in the adjacent diagram.

The shaded piece is a square of plate glass, half an inch

thick, with a square space worked out of it as shown in the figure. In contact with this frame, and covering its two faces, are two panes of thin plate glass, which are kept closely and firmly united to the frame by a small metallic press. The conductors in the cell are two balls of brass, electroplated with platinum, and attached each to a stiff wire, which passes upwards through an insulating tube of glass. These tubes



are supported by a stand (shown in the figure). The cell and stand are placed on an iron tripod, and enveloped by a wide muffle of sheet iron, with an aperture at the top for the long conductor, and two apertures at the sides for transmission of the light. Under the floor of the tripod is an Argand gas-burner, which supplies a current of hot air to the interior of the muffle.

In the course of some preliminary experiments on the fats and waxes, the fusion-cell was found to be not nearly so delicate as the plate cell, both instruments working under ordinary conditions—the former at high temperatures, the latter at the

temperature of the laboratory. The conditions of experiment with the fusion-cell are always in some degree unfavourable; so that a moderately strong effect obtained with this instrument may be accepted safely as an evidence of high electro-optic power in the dielectric. This remark applies to several important bodies (phosphorus, cetyl and cinnyl alcohols, spermaceti, &c.), which have given good effects in the fusion-cell.

### *Elementary Bodies.*

3. Bromine, phosphorus, and sulphur, all in the liquid state, are found to be electro-optically active and purely positive.

*Bromine* was examined in the plate cell without effect; but this trial was indecisive, as the plate of liquid was almost opaque to the sunbeam. I therefore had a special cell constructed, shaped like the fusion-cell, but only a quarter inch thick. As inductive terminal I used the long conductor of the fusion-cell, supported by its proper stand; the other conductor was a rounded segment of a disk of brass, resting on the floor of the cell, and connected by a lateral wire to earth. All the metallic pieces were plated with platinum; and the fumes from the liquid were sufficiently confined by a covering of soft leather pressed lightly on the mouth of the cell. The optical conditions were now very favourable. The image of the sun in the mirror of a *porte-lumière*, viewed through the centre of the electric field, was of course deeply coloured and much weakened; but it still presented a fine object in the polariscope: the extinction also was pure and sharp; and the object was well restored by a very feeble strain of the hand-compensator.

Tried as a nonconductor, the plate of bromine gave no optical effect; nor did it give any sensible spark in the test for insulation. Tried then as a conductor, with moderate charges of the jar, it gave a regular and very fine restoration, vivid and undistorted, and not at all abrupt. When tested by the hand-compensator, the effect was found to be purely positive, strengthened by tension parallel to the lines of force, and weakened to extinction by compression.

*Phosphorus* was examined in the fusion-cell, at a temperature a little above its melting-point. Several trials were made before a sufficiently clean plate was obtained; but I succeeded at last, by pressing out the phosphorus through a bag of chamois-leather, under hot water. The cell, charged nearly full with phosphorus, and then filled up with water, was placed in the hot-air bath, between the two Nicols; and the experiment was carried forward as in the case of bromine. The conditions of optical observation were unfavourable, the cell-panes being strongly and not very regularly strained by the heat.



The initial extinction was very slow and impure ; but it was perfected by careful regulation of the temperature, and by the application of a stationary neutralizing plate of glass. Like difficulties occurred in most of the experiments with the fusion-cell, and they were generally overcome in the same way.

Tried as a nonconductor, the plate of phosphorus gave no optical effect. Tried then as a conductor, with moderate charges of the jar, it gave a good restoration,—not so strong, I thought, as that of bromine, but equally regular and pure, strengthened by tension parallel to lines of force, and weakened to extinction by compression. Phosphorus therefore, like bromine, is purely positive.

Judging from some facts that presented themselves in the course of my experiments with fused phosphorus, I am almost sure that, with better apparatus and proper arrangements, this body would give a good optical effect as a nonconductor.

*Sulphur*.—The fusion-cell was placed on its tripod between the crossed Nicols, and all the pieces were put in final position as for the optical experiment ; the cell was then filled with sublimed sulphur, and the temperature of the air-bath was raised gradually. As the sulphur melted, new quantities were supplied till the cell was nearly full of liquid. The initial extinction was now restored as quickly as possible by the use of a thick neutralizing plate of glass placed in front of the second Nicol, and the sulphur was tried as a nonconductor. When the machine was set in motion, the flame was restored strongly from extinction ; and the effect was found to be purely positive, strengthened by tension parallel to lines of force, and extinguished by compression. As the experiment went on for a minute or more, the effect became weaker and weaker till it was imperceptible. The insulation had evidently failed, the temperature being too high for the apparatus.

The Leyden jar being now introduced quickly, the sulphur was tried as a conductor, and there was a strong restoration obtained by discharge at every fifth turn of the plate. The effect was still purely positive, strengthened by tension parallel to lines of force, and extinguished by compression. In a few minutes this effect also disappeared ; and it could not be recovered by regulation of the temperature. In the meantime the plate of sulphur had deteriorated very much from its first purity. Perfectly clean at first, it was now filled with black particles.

After this first experiment, I made several attempts to obtain a more constant effect, but without success. The conditions of the experiment were too trying for the apparatus : the cell was damaged in the first experiment, and was very soon de-

stroyed. Although I never recovered any thing like the very strong and fine effects which I have described, I have no doubt that fused sulphur is purely and strongly positive.

### *Hydrocarbons.*

4. Those of the hydrocarbons that I have examined up to this time, the nine or ten mentioned in my former paper, and the eight which here follow\*, are all nonconductors, electro-optically active, and purely positive.

*Amyl hydride*,  $C_5H_{12}$ , is interesting as one of the lightest of known liquids. Tested for insulation in the plate cell, it gave a spark hardly  $\frac{1}{4}$  inch long. Tried optically as a non-conductor, it gave a sure but extremely faint restoration from pure extinction. When the hand-compensator was introduced beforehand, and strained steadily, the effect of electric force was brought out more strongly, and with great purity—an increase of light in the case of tension parallel to lines of force, and a decrease to extinction in the case of compression. There was no increase of effect when the liquid was tried as a conductor, with or without the Leyden jar.

*Hexyl hydride*, or trityl,  $C_6H_{14}$ . For a specimen of this liquid, prepared from petroleum-oil, I am indebted to the kindness of Dr. Gladstone. It was examined immediately after amyl hydride, for the purpose of comparison. Of the two, the hexyl compound appeared to be somewhat stronger both in insulating and in electro-optic power. Both bodies exert very faint but perfectly pure actions as positive non-conductors.

*Cinnamol*,  $C_8H_8$ , tried in the plate cell as a nonconductor, gave an intense and purely positive effect. The action was strong enough to give definite and very black extinction-bands, like those in my old experiments with  $CS_2$  and the stronger hydrocarbons.

*Caprylene*,  $C_8H_{16}$ , acts in the plate cell as a positive non-conductor. Most of the plates of this liquid were somewhat dirty, and easily traversed by spark discharge; but the effect was always manifest, and always purely positive. In the cleaner plates the action was very fine, and apparently a good deal stronger than that formerly observed in the lighter olefine, amylenes.

*Caoutchoucine*, or empyreumatic oil of caoutchouc.—My specimen of this liquid was of a deep red colour, and a moderately good insulator; so that it could be tried in the plate cell

\* All of them pure hydrocarbons, except caoutchoucine and oil of resin, which contain a little oxygen.

as a nonconductor. The optical conditions were unfavourable, and the effect of electric force could hardly be detected from pure extinction; but when the hand-compensator was used (as with amyl hydride formerly), the effect came out very clearly—an increase of light in the case of tension parallel to lines of force, and a decrease to sensible extinction in the case of compression.

*Oil of Resin* is interesting for its great density,  $\cdot 9989$ . It is a distillate of common resin, redistilled from caustic potash, and is now largely used in the jute-manufacture. My specimen was a very clean trade-sample, of a clear amber-colour, a pretty strong photogyre, and a good insulator. Tried in the plate cell as a nonconductor, it gave a strong positive effect. As soon as the machine was set in motion, the light was restored from a faint red or blue, which was the best extinction, to an intense and sensibly pure white; and the effect was strengthened by tension parallel to lines of force, and weakened to good extinction by compression. This result agrees with my former observations on solid resin, where also the effects were positive, though very much fainter.

*Paraffin* fuses into a purely transparent liquid at about  $50^{\circ}$  C. Tried in the fusion-cell as a nonconductor, it gave a strong regular effect. A quarter turn of the plate restored the light well from extinction; and the effect was strengthened by tension parallel to lines of force, and neutralized by compression. The sluggishness of rise and fall of optical effect was very manifest. There was also some disturbance, produced by movements in the liquid, when the machine was in motion.

*Naphthaline*,  $C_{10}H_8$ , fuses at a moderate temperature into a transparent and very volatile oil. Tried in the same way as paraffin, it acted very similarly. There was a greater disturbance by gross movements in the liquid; but the optical effect was regular and perfectly distinct, conspiring with tension parallel to lines of force, and neutralizing compression.

#### *Alcohols*, $C_n H_{2n+1} HO$ .

5. Of this series, the eight members corresponding to the following values of  $n$  were examined in order:—

16, 8, 5, 4, 3, 2, 1, 0.

The first six are purely negative, falling in power perceptibly and regularly from first to sixth; the seventh and eighth are purely but feebly positive.

*Cetyl alcohol* ( $n=16$ ) fuses into a transparent and nearly colourless plate, at or near  $50^{\circ}$  C. It was tried in the fusion-cell as a nonconductor, after the initial extinction had been

perfected by careful regulation of temperature and by the use of a neutralizing plate. One turn of the machine gave a strong restoration in the polariscope; and the effect was purely negative, being neutralized by tension of the hand-compensator in a direction parallel to the lines of force, and regularly strengthened by compression. Good results of the same kind were obtained with half a turn of the plate, and even with a quarter turn. When the electric force was intense, there was some disturbance produced by movements in the liquid. When the temperature was raised very high, the regular effect disappeared, probably from failure of the insulation; and when the temperature was lowered to the point of solidification, and particles began to appear in the liquid, the optical effect became irregular and very weak, and (on the whole) apparently positive. But when these exceptional temperatures were avoided, the action of this alcohol was seen to be constantly, strongly, and purely negative. All the following members of the series were examined in the plate cell, and at ordinary temperatures.

*Capryl alcohol* ( $n=8$ ) gave no spark in the test for insulation, and was inactive accordingly when tried as a nonconductor. Tried as a conductor, with the jar and two or three turns of the plate, it gave a brilliant effect, which was found to be purely negative, being strengthened by compression of the hand-compensator in a direction parallel to the lines of force, and neutralized by tension, weakened in fact from a high intensity down to perfect extinction. Tried then without the jar, by discharge at every turn or half turn of the plate, it gave a clear and pretty strong effect, always purely negative by both tests.

*Amyl alcohol* ( $n=5$ ) is weaker than the last, both in insulating and in electro-optic power; for when tried as a conductor, without the jar, it gave a mere suspicion of effect. Tried then with the jar, and two or three turns of the plate, it gave a pretty strong effect, which was found to be purely negative by one test, being strengthened by compression parallel to lines of force, but not sensibly affected by tension. The failure of the second test, weakening by tension, was evidently due to the great abruptness of the electro-optic action, the momentary darkening of a steady flame being less perceptible than a momentary brightening. If any proof of the truth of this explanation were required, it could be supplied by a simple form of experiment, which I may describe further on.

*Butyl alcohol* ( $n=4$ ) is weaker than the last. Tried with the jar, it gave a very good restoration by discharge at every tenth turn of the plate. Five turns, powerful formerly with

amyl alcohol, gave now no sensible effect. The electro-optic action was found to be purely negative, conspiring regularly with compression parallel to lines of force, and giving no sensible change (except an apparently instantaneous tremor of the flame) with tension.

*Propyl alcohol* ( $n=3$ ) shows an additional fall of power. Tried with the Leyden jar, it gave a good restoration, though not strong, with fifteen turns of the plate. Ten turns, powerful with butyl alcohol, gave now no sensible restoration from extinction. The effect was purely negative, strengthened always by compression parallel to lines of force, and not sensibly affected by tension.

*Ethyl alcohol* ( $n=2$ ), specific gravity  $\cdot 795$ , showed a large fall of power. With plate machine and strongest charges of the jar, it gave no sure trace of effect. With the large Ruhmkorff's coil, working in the usual way with oscillating rheotome, it gave a strong heat-effect almost at once. The rheotome was therefore worked by hand, separate discharges being taken at intervals of 1 or 2 seconds. At each discharge, there was a perfectly regular, but very faint, restoration from pure extinction. Tested by the hand-compensator with great care, the electro-optic action was found to be purely negative, regularly neutralized or much weakened by tension parallel to lines of force, and regularly strengthened by compression.

*Methyl alcohol* ( $n=1$ ), tried with strongest charges of the jar, gave an effect which was clear and regular, but too feeble to be characterized. Tried with separate discharges of the coil, it gave a faint restoration regularly from pure extinction. Tested by the hand-compensator with great care, the effect was strengthened regularly by tension parallel to lines of force, and neutralized or much weakened regularly by compression; so that this alcohol, contrarily to the preceding six, is distinctly and purely positive. As far as I could judge, the action was somewhat stronger than the contrary action of ethyl alcohol.

*Distilled water* ( $n=0$ ), tried with strongest charges of the jar, gave a clear effect, apparently better than that in methyl alcohol, but still too faint to be characterized. Tried with separate discharges of the coil, it gave a faint restoration regularly from pure extinction. The effect was found to be purely positive, strengthened by tension parallel to lines of force, and neutralized or much weakened regularly by compression. I thought the action rather stronger than that of methyl alcohol, and certainly not weaker. The experiment with one charge of water could not be continued well for any length of time, as the electro-optic field was obscured very soon by an ascending cloud of gases.



*Acids, C<sub>n</sub>H<sub>2n</sub>O<sub>2</sub>.*

6. Of the series of fatty acids, the seven members corresponding to the following values of  $n$  were examined in the plate cell at ordinary temperatures:—

8, 6, 5, 4, 3, 2, 1.

The first six are purely positive, the seventh feebly but purely negative; and they fall regularly in power from the first to the last.

*Caprylic acid* ( $n=8$ ), tried as a nonconductor, gave a faint but good restoration regularly from extinction. As a conductor, its action was much stronger; and when the jar was used, the effect of discharge at every second or third turn of the plate was very brilliant. The effect from weak to strongest was purely positive, strengthened by tension parallel to lines of force, and extinguished perfectly by compression.

I never obtained this liquid, nor indeed any of the following acids, in a state of perfect (optical) purity. After any amount of filtering, there were always some visible specks left, solid particles apparently of the acid itself, or of some chemically homologous matter.

*Caproic acid* ( $n=6$ ) is distinctly weaker than the last, but otherwise hardly distinguishable from it in experiment. As a nonconductor, it gave no satisfactory effect in the polariscope. Tried as a conductor, with or without the jar, it gave a fine restoration, which was very brilliant with strong discharges; and the effect, weak or strong, was always purely positive, strengthened by tension, and extinguished by compression.

*Valeric acid* ( $n=5$ ) acts as a weak photogyre, barely separating the red and blue at extinction. Tried as a conductor, without the jar, it gave a regular effect, which was merely strong enough to be characterized as purely positive. With the jar it gave a series of brilliant effects, always purely positive by both tests.

With either of these three acids, it is easy to obtain a large range of optical effects, from very intense to evanescent, in one experiment. The jar is well charged, say by twenty turns of the plate, and the discharging balls are brought at short intervals into instantaneous contact, so as to discharge the jar gradually and discontinuously through the cell. Working in this way with valeric acid, and with one moderate charge of the jar, I have counted up to about fifty good restorations in the polariscope.

*Butyric acid* ( $n=4$ ), tried as a conductor, but without the jar, gave an effect which was too faint to be characterized, showing a distinct fall of power in comparison with the last

acid. With the jar and two turns of the plate, the restoration was good, though still faint; with ten or fifteen turns it was brilliant. The effect was always strengthened by tension parallel to lines of force, and always extinguished perfectly by compression.

*Isobutyric acid*, examined immediately afterwards in the same way, acted very similarly, but was apparently stronger.

*Propionic acid* ( $n=3$ ) showed an additional fall of power—gave no clear effect without the jar and five or more turns of the plate. The effect of discharge at every tenth turn was moderately strong, and was found to be purely positive by both tests.

Temperature was observed to have a great influence on the action of this acid. In one experiment, the initial temperature happened to be about  $0^{\circ}$  C., and there was no effect obtained with less than twenty turns of the plate; but when the cell was now gently heated by exposure for a minute in front of the fire, the effect of discharge was certain at every third turn, and good at every fifth.

*Glacial Acetic acid* ( $n=2$ ) showed an additional fall of power. With the jar and ten turns of the plate, it gave an effect so faint as to be often uncertain. With fifteen turns, the restoration was clear and regular, though not yet strong. Tested by the hand-compensator at this or higher power, the effect was strengthened regularly by tension parallel to lines of force, but hardly or not at all affected (and certainly not strengthened) by compression. Acetic acid is seen thus to be purely positive, and a very weak insulator. The second test by the hand-compensator (neutralization by the proper strain), fails here, as it failed earlier (with Leyden discharges) in the series of alcohols.

*Crystallizable Formic acid* ( $n=1$ ) showed a large additional fall of power, with undoubted reversal of sign. Tried with plate machine and strongest charges of the jar, it gave an effect which was clear and perfectly regular, though very faint and abrupt. The light was now restored steadily and very faintly from extinction, by permanent strain of the hand-compensator; and the observations were repeated. In the case of compression parallel to lines of force, the effect was regular and very distinct; the light brightened sensibly for a moment at the instant of discharge. In the case of tension parallel to lines of force, the effect was not so regular; at the instant of discharge the light was sensibly and very abruptly darkened in a few instances, never certainly strengthened, and generally affected merely as by an instantaneous shock, without seizable change of intensity. Like results, though hardly so good, were obtained

afterwards with the Ruhmkorff's coil. Formic acid is therefore purely negative, but a very weak insulator. It gives no good effect at temperatures very near the freezing-point; and the same remark applies to acetic acid.

7. Two of the so-called solid acids of the same series were examined in the fusion-cell, and were found to be negative.

*Palmitic acid* ( $n=16$ ), a transparent oil at or above  $62^{\circ}\text{C}$ ., acted well as a nonconductor. One turn of the plate gave an intense restoration, whose purely negative character was very little disturbed by movements in the liquid. When the temperature was little above the point of fusion, and carefully regulated, the initial extinction was very good without the neutralizing plate, and there was no trace of disturbance by currents. One eighth of a turn gave then a good effect which was purely negative, strengthened by compression parallel to lines of force, and extinguished by tension.

*Stearic acid* ( $n=18$ ), a transparent oil at or above  $70^{\circ}\text{C}$ ., acted on the whole as well as the last, though there was rather more disturbance by currents. One turn of the plate gave always a strong effect which was purely negative, conspiring with compression parallel to lines of force, and neutralizing tension.

These results were very unexpected. I therefore tested them at some length, working with new samples of the acids, the purest that could be obtained, and comparing them successively with paraffin and the fats. The facts never varied: the two fused acids were always distinctly and purely negative.

#### *Other Alcohols and Acids.*

8. *Allyl alcohol*,  $\text{C}_3\text{H}_5\text{HO}$ , is distinctly though not quite purely negative, and a good deal stronger than ethyl alcohol. With good charges of the jar it gave a clear effect, which was strengthened by compression parallel to lines of force, and weakened almost to extinction by tension. There was always some disturbance produced, partly by a feeble photogyric action of the liquid, and partly by a special effect of electric discharge. The flame was not simply restored in the polariscope by discharge, but was deformed as by an undulatory movement in the liquid, and rendered also fibrous or thready in appearance. This effect was probably due to heat; for it came out much more strongly afterwards with the Ruhmkorff's coil, in which case three separate discharges were sufficient to mask the electro-optic action completely by a permanent heat-effect.

*Benzyl alcohol*,  $\text{C}_7\text{H}_7\text{HO}$ , is purely negative. Tried in the plate cell as a conductor, it gave a faint but good restoration

with five turns of the plate, strong with ten turns ; and the effect was purely negative.

*Cinnyl alcohol*,  $C_9H_9HO$ , is purely negative. Tried in the fusion-cell at a temperature a little above its melting-point,  $33^\circ C.$ , it acted well as a conductor. With ten turns of the plate it gave a clear and pretty strong effect, which was found to be purely negative by both tests.

*Glycol*,  $(C_2H_4)''H_2O_2$ , is very feebly and impurely negative. This is a very inconvenient liquid to work with, viscous and heterogeneous, giving permanent deformations of the flame, and impure initial extinction in the polariscope. With strongest charges of the jar, it gave a mere trace of effect, which appeared to be negative. With the strongest Ruhmkorff-discharges, the restorations were clearer, and almost perfectly regular, but still faint, and obscured by disturbance. The effect was pretty surely negative, strengthened sensibly by compression parallel to lines of force, but not extinguished by tension.

*Glycerin*,  $(C_3H_5)'''H_3O_3$ , is certainly, but feebly and impurely, negative. As far as I can judge from my samples, this liquid is more unsuitable even than glycol for delicate optical work. With the Ruhmkorff's coil, it acted better than glycol, giving very good restorations, notwithstanding great disturbance produced by the syrupy structure of the plate. The effect was found to be certainly negative, though the neutralizing action of tension was not always seized.

*Phenol*,  $C_6H_5HO$ , is purely positive. In the fusion-cell, at or above  $35^\circ C.$ , it acted well with the plate machine and without the jar, but required several turns of the plate. There was generally some optical disturbance by heterogeneous structure, and also by movements in the liquid, when the electric force was intense ; but the optical effect was regular and very distinct, purely positive by both tests.

*Oleic acid*,  $C_{18}H_{34}O_2$ , is purely and strongly positive. Tried in the plate cell as a non-conductor, it acted more intensely than any of the fatty acids—gave a regular and pretty strong effect, which was strengthened by tension parallel to lines of force, and extinguished perfectly by compression.

*Lactic acid*,  $C_3H_6O_3$ , is apparently positive. Tried with strongest charges of the jar, and afterwards with the coil, it gave a regular effect, undoubtedly pure, and pretty surely positive, but too faint and abrupt to be characterized with perfect certainty. The liquid was evidently a very weak insulator.

#### *Oxides*, $(C_nH_{2n+1})_2O$ .

9. The only two of these that have been examined are purely negative, and much stronger than the corresponding alcohols.

*Ethyl oxide* (purus, P.B.), tried as a conductor with machine and Leyden jar, gave a good restoration with eight turns of the plate, pretty strong with ten turns; and the effect was strengthened by compression parallel to lines of force, and regularly neutralized by tension. With the Ruhmkorff's coil afterwards, there was a good effect obtained even when the length of the safety spark was reduced to zero; and the action of the compensator was as clear as formerly, extinction by the proper tension being regularly perfect. This liquid is therefore purely negative, and a great deal stronger than ethyl alcohol.

*Amyl oxide*, tested for insulation in the plate cell, gave a strong spark ( $\frac{3}{4}$  inch) from the prime conductor. Tried optically as a nonconductor, it acted like the best of the fixed oils. As soon as the machine was set in motion, there was a strong effect from extinction, which was neutralized perfectly by tension parallel to lines of force. Among chemically definite bodies, I regard this amylic ether as the best negative dielectric yet discovered.

#### *Iodides, C<sub>n</sub>H<sub>2n+1</sub>I.*

10. Four of these were examined in the plate cell, first as nonconductors, but without effect, then as conductors. The regular effects were disturbed in some degree by photogyric action, but were all clearly positive.

*Methyl iodide*, without the jar, gave a good restoration, which was too quick to be characterized. With the jar and five or four turns of the plate, the effect was distinctly positive, strengthened by tension parallel to lines of force, but not sensibly affected by compression.

*Ethyl iodide* was of a deep red colour, much darker than the methyl compound, but otherwise not distinguishable from it in experiment.

*Butyl iodide*, still deeper in colour, and almost opaque, required the jar and fifteen or more turns of the plate. The effect was regularly strengthened by tension parallel to lines of force, but not sensibly affected by compression.

*Amyl iodide* was the strongest of the four. With the jar and three or even two turns of the plate, it gave a clear effect, which was strengthened by tension parallel to lines of force, and weakened to extinction by compression.

#### *Bromides, C<sub>n</sub>H<sub>2n+1</sub>Br.*

11. These are purely positive, the powers rising as  $n$  increases; and they are distinctly stronger than the corresponding iodides.

*Ethyl bromide*, tried as a conductor with the jar, gave a clear



but faint restoration with five turns of the plate, strong with ten turns ; and the effect was purely positive by both tests.

*Propyl bromide*, as a conductor, but without the jar, gave a good effect which was positive by one test, clearly strengthened by tension parallel to lines of force, but not sensibly affected by compression. With the jar, one turn of the plate gave a strong effect, which was purely positive by both tests.

*Isopropyl bromide* acted more strongly, giving a clear effect as a nonconductor. Tried as a conductor, with the jar, it gave increasingly brilliant restorations with two, five, ten, or more turns ; and the effect from weak to strongest was purely positive, strengthened by tension, and extinguished by compression.

*Butyl bromide*, not a very clean sample, was hardly so strong as the last, giving a mere trace of effect as a nonconductor. Tried as a conductor, with the jar, it gave a good restoration with one turn, strong with three turns ; and the effect was purely positive by both tests.

*Amyl bromide*, tried as a nonconductor, was quite inactive at first, giving no trace of effect in the polariscope, no sensible spark from the prime conductor ; but when the machine had worked for a little time, the optical effect came out clearly, and was found to be purely positive. Tried then as a conductor, with the jar, it gave a splendid restoration with one turn of the plate. When the jar was detached, well charged, and again connected for discharge through the cell, the light flamed up in the polariscope with great brilliancy, and faded away gradually, remaining visible for sixty or more seconds. The increase of insulating and electro-optic powers of the dielectric in the course of this experiment, and in a few minutes of time, was very remarkable.

#### *Chlorides, $C_nH_{2n+1}Cl$ .*

12. These are purely positive, and stronger than the bromides ; and they show a great increase of power as the experiment proceeds.

*Propyl chloride*, tried in the plate cell as a nonconductor, gave at first no trace of effect in the polariscope, no sensible spark from the prime conductor. Tried then as a conductor, it gave a clear and strong restoration at each discharge. When the jar was added, one, two, three, or more turns gave increasingly brilliant effects, which were found to be purely positive by both tests. When the observations had been carried on for some time, the liquid was tried again as a nonconductor. The prime conductor gave now a spark fully a quarter of an inch long ; and the polariscope gave a

fine effect, purely positive. The final action was at least as strong as that of amylene. My sample of this liquid was not very clean; and the initial extinction was far from pure.

*Butyl chloride* was rather weaker than the last, and showed no great increase of power with time. As a conductor, without the jar, it gave a good restoration which was too abrupt to be characterized; with the jar and four or five turns of the plate, it gave a very strong effect, purely positive by both tests. My sample was not clean; and the initial extinction was quite impure.

*Amyl chloride*, a very fine optical medium, giving perfect initial extinction. As a nonconductor, it gave at first no trace of effect in the polariscope, no spark from the prime conductor. Tried then as a conductor without the jar, it gave a clear restoration, too abrupt at first to be characterized; but as the experiment went on, the machine working at a moderate rate, and discharges passing regularly through the cell, the restorations in the polariscope rose very gradually in intensity, till at last the effect was one of the finest that I had ever seen. The liquid being now tried again as a non-conductor, the prime conductor gave a spark more than half an inch long, and the electro-optic action was magnificent, as fine apparently as that of  $\text{CS}_2$ . The effect was always strengthened by tension parallel to lines of force, and always weakened to extinction by the proper compression.

[To be continued.]

XIX. *Researches on Chemical Equivalence.*—I. *Manganous and Nickelous Sulphates.* By EDMUND J. MILLS, D.Sc., F.R.S., and J. H. BICKET\*.

THE following experiments were conducted with the view of determining on what terms manganous and nickelous sulphates might prove to be mutually equivalent; and the particular equivalence we have examined has been equivalent precipitability of the sulphates, by sodic carbonate, from an aqueous solution.

I. *Preparation of the Salts.*

The pure manganous sulphate was prepared from the ordinary commercial dioxide. The oxide was dissolved in hydric chloride, the solution filtered and evaporated to dryness, the residue dissolved in water, and excess of baric carbonate added

\* Communicated by the Authors.

to precipitate the iron; the barium was separated by hydric sulphate; and the manganese was precipitated from the solution by means of sodic carbonate. The manganous carbonate thus obtained was well washed with water, dissolved in hydric chloride, and baric carbonate again added in order to precipitate any remaining traces of iron. After the barium had been removed with hydric sulphate, the manganese was again thrown down as carbonate with sodic carbonate. The manganous carbonate, after being well washed and dried, was roasted; and the oxide obtained was washed with dilute hydric nitrate to remove any sodic salt. As the oxide obtained was very slightly acted on by hydric sulphate at any temperature or of any strength, we could not obtain the sulphate by the direct action of hydric sulphate on this oxide. The oxide was therefore dissolved in hydric chloride, the solution evaporated to dryness, and ignited with excess of strong pure hydric sulphate. This ignition with hydric sulphate having been repeated, the salt was found to be free from all impurities, and quantitative analysis showed it to be pure anhydrous manganous sulphate.

The pure nickelous salt was prepared from a sample of nickelous chloride which contained copper, lime, and iron, but no cobalt. The copper present was precipitated with hydric sulphide; and the nickel in the filtrate was precipitated by hydric oxalate in an acid solution. The nickelous oxalate was washed thoroughly with dilute hydric nitrate, ignited, and the oxide so obtained heated with pure hydric sulphate and so converted into sulphate.

The sodic carbonate was prepared by igniting hydrosodic carbonate in a double platinum crucible, dissolving in water, and reprecipitating with carbonic dioxide, igniting this as before, and repeating the operation. The final precipitate was dissolved in boiling water to the necessary strength.

## II. *Method of separating Nickel from Manganese.*

The method for the separation of manganese from nickel that we found to give the most accurate results was that of Beilstein and Jawein\* for the separation of manganese from iron. It consists in evaporating the mixed solutions to dryness, adding strong pure hydric nitrate, heating to boiling, and adding potassic chlorate in small quantities at a time. The manganese is thus precipitated as pure black oxide; which, after filtering and washing free from the nickel that is in solution, is dissolved in hydric chloride, precipitated with sodic phosphate, and ignited and weighed as manganous pyrophos-

\* *Deut. chem. Ges. Ber.* 1879, p. 1528.

phate. The nickel solution is evaporated to dryness (to get rid of the large excess of acid), dissolved in water, and precipitated as sulphide with ammoniac sulphide. The sulphide is then ignited with excess of pure hydric sulphate in an open porcelain crucible, and weighed as nickelous sulphate.

In experiments that were tried to ascertain the accuracy of this method, the following results were obtained:—Two solutions, each containing 0·2500 grm. manganous sulphate and 0·2500 grm. nickelous sulphate, were taken; the manganese was separated by the method given above, with the following results:—

(a) Manganous sulphate obtained . . . . .	=0·2506
Nickelous sulphate . . . . .	0·2503
(b) Manganous sulphate obtained . . . . .	0·2497
Nickelous sulphate . . . . .	0·2517
Mean . . . . .	0·2506

Having now fixed on the method for separation that was to be used, we made up solutions of the salts required.

For the manganous and nickelous sulphates, 1-per-cent. solutions were made. The sodic carbonate solution was of 5·7151 per cent. strength. It was kept in a stoppered bottle that had been well coated internally with paraffin.

### III. A. Conjoint Precipitability.

A series of nine experiments was made, in which the relative weights of nickelous or manganous sulphate present varied from ·1 to ·9 grm.,—the total weight of nickelous and manganous salt and the volumes of the solution being, however, always the same, viz. 1 grm. and 100 cub. centim. The experiments were conducted as follows:—The bottles containing the solutions of the sulphates and the sodic carbonate were immersed in a tank, through which there was a constant flow of water from the main to bring them to a constant temperature. The necessary quantities of nickelous and manganous solutions were then carefully measured out, mixed, and the temperature observed. 10 cub. centim. of sodic carbonate solution were then added, the mixture stirred, and the temperature again observed. The precipitate was then filtered off as quickly as possible\* (an aspirator being used to facilitate the filtration) and washed, first with cold and then with hot water.

\* Continued experience with precipitation experiments has convinced us that our probable error would have been less if we had allowed the precipitate to stand some time.

The washing of the precipitate took a long time (a maximum of two days), especially when the nickelous salt was in excess of the manganous. After the precipitate had been washed, it was dissolved in dilute hydric chloride, and the manganese and nickel separated and estimated by the method given above.

In the course of these experiments we noticed that, (1) if we kept the clear filtrate in a glass-stoppered bottle for some time, or boiled it, a further precipitate appeared; and (2) that the clear filtrate was alkaline to test-paper, turning red litmus blue.

The results obtained in these experiments are comprised in the following table ("temperature" meaning temperature of the reagents *after* mixture):—

TABLE I.

Nickelous salt taken. <i>n.</i>	Manganous salt taken. <i>m.</i>	Nickelous salt precipi- tated. <i>v.</i>	Manganous salt precipi- tated. <i>μ.</i>	Temperature.
gram.	gram.	gram.	gram.	
·1000	·9000	·0953	·5850	12·9 C.
·2000	·8000	·1852	·4616	13·6
·3000	·7000	·2799	·3766	12·5
·4000	·6000	·3588	·2976	13·0
·5000	·5000	·4305	·2450	13·6
·6000	·4000	·4788	·1536	12·8
·7000	·3000	·4991	·1089	17·0
·8000	·2000	·5584	·0722	17·0
·9000	·1000	·5841	·0363	15·2

### III. B. *Separate Precipitability.*

We next tried the following experiments to determine the precipitability of manganous and nickelous sulphates when separate. Four series were undertaken, viz. (1) when the nickelous salt varied and the sodic carbonate was constant, (2) nickelous salt constant and sodic carbonate varying, (3) manganous salt varying and sodic carbonate constant, (4) manganous salt constant and sodic carbonate varying.

(1) *Nickelous Salt varies, Sodic Carbonate constant.*—The bottles containing the solutions were brought to a constant temperature by immersion in a tank of running water. After the solution of nickelous sulphate had been measured out, it was made up to 100 cub. cent. with distilled water that had been cooled to the same temperature, and then 10 cub. cent. of the sodic carbonate solution was added, the mixture stirred,



and the temperature observed. The precipitate was then filtered (with the help of an aspirator), and washed with cold and afterwards with hot water until the washings showed no trace of nickel; the precipitate was then dissolved in pure hydric sulphate, evaporated to dryness, ignited, and weighed as nickelous sulphate. The results obtained in these experiments are given in the following table:—

TABLE II.

Sodic carbonate taken. <i>x.</i>	Nickelous salt taken. <i>x.</i>	Nickelous salt (obtained) precipitated. <i>y.</i>	Nickelous salt (calculated) precipitated.	Temperature.
gram. 0.57151	gram. 0.1050	gram. 0.1015	gram. 0.1192	5.6 C.
"	0.2100	0.1912	0.2139	4.8
"	0.5000	0.4084	0.3967	7.3
"	0.7100	0.5103	0.4856	4.8
"	1.0000	0.5550	0.5745	5.6

(2) *Nickelous Salt constant, Sodic Carbonate varies.*—This series was conducted in the manner of (1); only there was always the same volume of nickelous sulphate measured out, viz. 100 cub. cent. To this was added enough distilled water to make, along with the volume of sodic carbonate to be added, 10 cub. cent. The results thus obtained are given in the following table:—

TABLE III.

Sodic carbonate taken. <i>x.</i>	Nickelous salt taken.	Nickelous salt (obtained) precipitated. <i>y.</i>	Nickelous salt (calculated) precipitated.	Temperature.
gram. 0.057151	gram. 1.000	gram. 0.0300	gram. 0.0393	7.8 C.
0.114302	1.000	0.0798	0.0810	8.1
0.285755	1.000	0.2311	0.2242	7.9
0.571510	1.000	0.5438	0.5450	7.9

(3) *Manganous Salt varies, Sodic Carbonate constant.*—The manganous sulphate was measured out, the solution made up to 100 cub. cent. with distilled water, and 10 cub. cent. of sodic carbonate solution added; the mixture was then stirred, and the precipitate filtered off, washed, and dissolved in pure hydric chloride. The manganese was estimated as pyrophosphate. The results were as follows:—

TABLE IV.

Sodic carbonate taken.	Manganous salt taken. <i>x</i> .	Manganous salt (obtained) precipitated. <i>y</i> .	Temperature.
gram. 0.57151	gram. 0.1050	gram. 0.1039	9.3 C.
"	0.2000	0.1969	9.3
"	0.5000	0.4894	10.1
"	0.7100	0.6748	10.1
"	1.0000	0.7500	9.7

(4) *Manganous Salt constant, Sodic Carbonate varies.*—This series was conducted like series (2). The washed precipitate was dissolved in hydric chloride and the manganese estimated as pyrophosphate. The results are given in the following table:—

TABLE V.

Sodic carbonate taken. <i>x</i> .	Manganous salt taken.	Manganous salt (obtained) precipitated. <i>y</i> .	Manganous salt (calculated) precipitated.	Temperature.
gram. 0.057151	gram. 1.0000	gram. 0.0400	gram. 0.0577	7.6 C.
0.114302	1.0000	0.1145	0.1188	7.6
0.285755	1.0000	0.3558	0.3261	7.8
0.57151	1.0000	0.7592	0.7797	9.2

### Discussion.

*Conjoint Precipitability.*—If  $n$  represent nickelous sulphate taken, and  $v$  the carbonate (calculated to sulphate) obtained from it by precipitation, then  $\phi$  in the expression  $n = \phi v$  is the precipitability. Our experiments (Table I.) satisfy the equation

$$\phi = 98570 + 61438n. \quad (1)$$

(which is deduced from all of them), with a probable error of 0.055284 for a single determination, or 0.018428 for nine determinations.

Similarly, in the case of manganous sulphate (Table II.),

$$\phi = 3.0881 - 1.7203m; \quad (2)$$

with probable error amounting to 0.088893 and 0.029631 respectively. In both cases, therefore, the precipitability is a linear function of the mass. The second constants in equations (1) and (2) present an interesting relation, closely resembling that

which we have elsewhere\* shown to hold good for nickelous with cobaltous sulphate. Within the limits of error of experiment, the second constant in (1) is the reciprocal of the second constant in (2). The attraction of nickelous sulphate for the reagent is thus the inverse of that of manganous sulphate.

In order to ascertain in what proportions the commixed sulphates are equally precipitable, we have

$$\cdot 98570 + \cdot 61438n = 3\cdot 0881 - 1\cdot 7203m,$$

whence

$$m = 1\cdot 2221 - \cdot 35714n.$$

This equation does not admit of solution except on some further supposition with respect to  $m$  or  $n$ . Now Table I. shows that the required values of  $m$  or  $n$  are very nearly equal to 0·9, and consequently that equal weights of nickelous and manganous sulphates are equally precipitable. If, in fact, in the equation just given we put  $n=0\cdot 9$ , we shall find the substantially identical value 0·9007 for  $m$ .

To calculate in what proportions the two sulphates must be mixed so that they may give equal weights of precipitate, we have

$$\frac{n}{m} = \frac{(\cdot 98570 + \cdot 61438n)\nu}{(3\cdot 0881 - 1\cdot 7203m)\mu} \}$$

$$n = 1 - m.$$

Putting  $\frac{\nu}{\mu} = 1$ , and combining these equations, we obtain a quadratic, one of whose solutions is  $m = \cdot 6215$ , and consequently  $\nu = \cdot 3785$ . Substituting these values in the primitive equations, we find  $\mu = \cdot 3086$ ,  $\nu = \cdot 3107$ —very nearly equal weights.

*Separate Precipitation.*—In cases of precipitation of a single salt, if  $x$  be the weight of reagent taken,  $y$  the weight of precipitate obtained, and  $\alpha$ ,  $\beta$  constants of condition, some form of the relation

$$y = \frac{\beta x}{1 + \alpha x} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

is ordinarily valid. The sign of  $\beta$  is necessarily positive; but the sign of  $\alpha$  depends upon the order of constancy in precipitation. The equation can obviously apply only as long as

$\phi = \frac{x}{y}$  is  $\leq$  or  $> 1$ . There are very few instances in which, as when sodic chloride acts on argentic nitrate in a weak solution, the

\* Proc. Roy. Soc. xxix. 181.

value of  $\alpha$  vanishes and  $\beta$  represents an undisturbed combining proportion.

In Table II. we have stated the result of acting upon a constant quantity of sodic carbonate with a varied amount of nickelous sulphate. The equation employed in the calculation, all experiments being taken into account, is

$$y = \frac{1.2816x}{1 + 1.2308x} \quad \dots \quad (4)$$

Probable error of a single experiment, .014915. Applying the criterion as to  $\phi$ , we notice that the equation cannot actually hold good until  $x = .2288$ , though the difference between theory and experiment is not great before that stage.

On the other hand, when (Table III.) nickelous salt is kept constant and sodic carbonate is the varied precipitant, we have

$$y = \frac{.66641x}{1 - .52700x}, \quad \dots \quad (5)$$

with a probable error .0046138 for a single experiment. Similarly, when carbonate is constant and manganous salt varies (Table IV.),

$$y = \frac{2.7486x}{1 + 2.6648x}, \quad \dots \quad (6)$$

an equation which is not rational until  $x = .6562$ , and has therefore been necessarily calculated from the last two experiments only.

Again, when manganous salt is constant and carbonate varies (Table V.),

$$y = \frac{.98103x}{1 - .49146x}; \quad \dots \quad (7)$$

the probable error of a single experiment being .015742.

If in equation (3) we put  $\phi = \frac{x}{y}$ , we shall find that

$$\phi = \frac{1 + \alpha x}{\beta},$$

a relation which, when we adopt other constants, may be expressed as follows:—

$$\phi = a + bx.$$

Hence the precipitability equation is, as we have already seen, a linear one.

The equation to  $\phi$ , as thus deduced from the separate precipitation experiments [ $\phi_s$ ], differs in its constants from that to which the "conjoint" experiments [ $\phi_c$ ] have led us. The

two equations are apparently related thus

$$\phi_c = a + bx,$$

$$\phi_s = (a + p) + (b - p)x,$$

where  $p$  is some constant to be deduced from the determinations. We find, in the case of manganous sulphate, that these relations do in fact hold accurately; but the results with nickelous sulphate are not in definite accordance with them. We trust on some future occasion to resume the consideration of this subject, which is of primary importance in the theory of precipitation.

The equations of separate precipitability (as deduced from the separate precipitation experiments) are

$$\phi_m = \cdot 36383 + \cdot 96951m, \quad . \quad . \quad . \quad (8)$$

$$\phi_n = \cdot 78027 + \cdot 95815n. \quad . \quad . \quad . \quad (9)$$

Here there is no reciprocal relation between the second constants, which are indeed identical within the limits of experimental error. We infer from these numbers that manganous and nickelous sulphates, when separate, are equally precipitable.

The following are the chief conclusions which we have drawn from our work.

1. Precipitability is a linear function of mass.
2. When commixed manganous and nickelous sulphates are precipitated by sodic carbonate, equal weights of them are equally precipitable, the attraction of one of them for the reagent being the inverse of that of the other.
3. When the above sulphates are separately precipitated by the same reagent, they are equally precipitable, and do not exhibit the inverse function.
4. There is some evidence that the precipitabilities of the commixed and separate sulphates are mathematically related in a simple manner.
5. Within moderate limits, precipitation is not traceably affected by temperature.

XX. *Researches on Chemical Equivalence.*—II. *Nickelous and Cadmic Sulphates.* By EDMUND J. MILLS, D.Sc., F.R.S., and BERTRAM HUNT\*.

WE propose to consider a case in which a metallic sulphate belonging to some other group is compared with nickelous sulphate (the previously employed standard), sodic carbonate being the precipitant. For this purpose we have selected cadmic sulphate—partly because it admittedly

\* Communicated by the Authors.



fulfils the required condition, and partly because it nevertheless has some strong analogies with the nickel group.

### I. *Preparation of the Salts.*

Pure cadmic sulphate was prepared from an excellent commercial sample, the only impurity in which was a small quantity of zinc sulphate. From an acidified aqueous solution of the sample, cadmic sulphide was thrown down by hydric sulphide. The washed sulphide was then dissolved in pure hydric sulphate, and rendered neutral by careful ignition.

1-per-cent. solutions of each of these salts were accurately prepared. The sodic carbonate solution was prepared and treated as in Part I.\*

### II. *Separation of Nickel from Cadmium.*

From a solution of the mixed chlorides, cadmic sulphide was precipitated as sulphide; this was washed, dissolved in strong hydric chloride, evaporated with hydric sulphate, ignited and weighed as sulphate. The filtrate and washings were also evaporated with hydric sulphate; the ignited residue was weighed as nickelous sulphate.

### III. *Precipitability Experiments.*

The solution of pure sodic carbonate was of such a strength that 1 cub. cent. of it exactly corresponded ( $\text{Na}_2\text{O}_3 : \text{CdSO}_4$ ) to 1 cub. cent. of the cadmic solution. The usual series of nine experiments was made, under the same general conditions as in Part I.—the constant weight of mixed metallic sulphates being 1 grm., and volume of their solution 100 cub. cent., the constant volume of carbonate solution being 100 cub. cent. The precipitates were in all cases allowed one hour's repose; they were then filtered as rapidly as possible with the aid of an aspirator, and washed with cold water. The results are given in the following table, the precipitate being returned as sulphate:—

Nickelous sulphate taken. <i>n.</i>	Cadmie sulphate taken. <i>d.</i>	Nickelous sulphate precipitated. <i>v.</i>	Cadmie sulphate precipitated. <i>ê.</i>	Temperature.
·9	·1	·5705	·0810	° 7·0 C.
·8	·2	·5351	·1823	7·0
·7	·3	·4477	·2763	10·4
·6	·4	·3875	·3546	12·0
·5	·5	·3295	·4807	9·6
·4	·6	·2563	·5937	10·0
·3	·7	·1876	·6990	10·5
·2	·8	·1358	·8010	10·7
·1	·9	·0692	·9037	11·3

\* For Part I. see *antè*, p. 169.

IV. Discussion.

The precipitability of nickelous sulphate being, as heretofore, represented by  $\phi = \frac{n}{\nu}$ , we find our experiments in accordance with the equation

$$\phi = 1.53106. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Probable error of a single experiment, .034802; of nine experiments, .011601.

In a similar manner, the precipitability of cadmic sulphate,  $\phi = \frac{d}{\delta}$ , proves to be

$$\phi = 1.19462 - .25763d. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Probable error of a single experiment, .025793; of nine experiments, .008598.

In order to ascertain under what conditions the two sulphates are equally precipitable, we must have

$$1.19462 - .25763d = 1.53106,$$

which leads to  $-1.3059$  as the value of  $d$ . To this negative result no chemical interpretation can be assigned. We consequently infer that, in these experiments, *nickelous and cadmic sulphates are not comparable in point of precipitability*.

To calculate in what proportions the sulphates should be mixed in order to yield equal weights of precipitate, we must solve the quadratic

$$\left. \begin{aligned} \frac{n}{d} &= \frac{1.53106\nu}{(1.19462 - .25763d)\delta} \\ n &= 1 - \delta \end{aligned} \right\}$$

[The condition gives  $\frac{\nu}{\delta} = 1$ ]. The deduced values are  $d = .4153$  and  $n = .5847$ . Inserting these quantities in the primitive equations, we obtain  $\nu = \delta = .3819$ , a result evidently in accordance with experiment.

Our present inference with regard to the precipitability of nickelous-cadmie salt will lead (if confirmed by the action of reagents other than sodic carbonate) to the following important criterion:—*Two elements belong to the same group when, in saline solutions of identical genus, they may be equally precipitable.*

**XXI. Chemical Symmetry, or the Influence of Atomic Arrangement on the Physical Properties of Compounds.** By THOMAS CARNELLEY, D.Sc., Professor of Chemistry in Firth College, Sheffield.

[Concluded from p. 130.]

**II. INFLUENCE OF ATOMIC ARRANGEMENT ON THE SOLUBILITY.**

WE have seen that those compounds whose atoms are symmetrically arranged melt higher than those in which the arrangement is asymmetrical. Now let us see if there are not other physical properties which vary in this respect in the same way as the melting-point.

All bodies are acted on by at least two forces; one of which is the attraction between the molecules, and the other (*viz.* heat) tends to drive them apart. When the first force is in excess of the second, the body is solid; when the second is in excess, the body is a gas; when the two are about equally balanced, the body is liquid. Therefore the greater the attraction between the molecules the greater the temperature required to melt the body, and consequently the higher the melting-point. Having come to this conclusion, let us see if there are not other physical properties which depend on the attraction between the molecules, and which hence ought to be affected by symmetry of arrangement of the atoms in the molecule in the same way as the melting-point.

The first of such properties which suggests itself is solubility. In order that a solid may dissolve in any liquid, it is necessary that its molecules should undergo a sort of unloosening process; and we should therefore conclude that, of two isomeric compounds, that would dissolve the most easily in which the attraction between the molecules was the least, and which would therefore, as shown above, have the lowest melting-point. This argument shows, then, *that of two isomeric bodies that dissolves the most easily which has the lower melting-point, and in which therefore the atomic arrangement is less symmetrical.*

Let us now apply this rule in a few cases, and see whether symmetrical compounds are less soluble than their asymmetrical isomers. The following instances were taken quite promiscuously from Watts's 'Dictionary,' and are all that were tried, whether agreeing or not with the rule. The numbers in the third column represent the *order* of solubility; whilst the melting-point is taken as a measure of the symmetry:—

		Melting-point.	Order of solubility.	Remarks.
Diphenyl ben- zene, $C_6H_5Ph_2$ }	(1.2 or 1.3) (1.4)	85 205	1 2	} In alcohol, ether, $CS_2$ or $C_6H_6$ .
Phthalic acid, $C_6H_4(COOH)_2$ }	..... { 1.2 1.3 1.4	175 a 300 does not melt.	? 1 2	
Dinitrobenzene, }	..... { 1.3 1.2 1.4	89 118 171	1 2 3 (?)	} In alcohol, benzene, or chloroform.
Dichlorbenzoic acid, $C_6H_3Cl_2COOH$ }	{ 1.3.4 1.2.3 or 1.2.5 1.2.4	126 156 201	1 2 3	
Chlorbenzoic acid, }	{ 1.2 1.3 1.4	137 152 234	1 2 3	} In water.
Brombenzoic acid, }	{ 1.2 1.3 1.4	147 155 250	1 2 3	
Nitrobenzoic acid, }	{ 1.2 1.3 1.4	143* 142 240	1 2 3	} In water.
Nitrobrombenzoic acid, }	{ 1.2.5 1.2.3	140 250	1 2	
Amidobenzoic acid, $C_6H_4NH_2COOH$ }	{ 1.2 1.3 1.4	144 173 186	1 2 3	} In water.
*Oxybenzoic acid, }	{ 1.2 1.3 1.4	156 200 210	2 ? 1	
Methoxybenzoic acid, $C_6H_4OCH_3COOH$ }	{ 1.2 1.3 1.4	99 106 175	1 1 3	} In water.
*Oxybrombenzoic acid, }	{ 1.2.5 1.2.3	164 219	2 1	
Pyridine monocarboxylic acids:—				
Picolinic acid .....		135	1	} In water.
Nicotinic acid .....		228	2	
Pyridine dicarboxylic acids .....	{ $\gamma$ $\beta$ $\alpha$	237 243 245	1 2 3	} In water.

Table (continued).

	Melting-point.	Order of solubility.	Remarks.	
	Amide.		Ba salt.	Pb salt.
†Toluene sulphonic acids, $C_6H_4.CH_3.SO_3H$ { 1.3 1.4 1.2	108 136 154	1 2 3	1 2 3	1 2 3
Isostilbene, $CH_2=C(C_6H_5)_2$ .. Stilbene, $C_6H_5.CH=CH.C_6H_5$	Liquid. 120	1 2	} In alcohol.	
Ditolyl, $CH_3.C_6H_4.C_6H_4.CH_3$ { 1.2; 1.4 1.4; 1.4	Liquid. 121	1 2	} In alcohol.	
Dinaphthyl ..... { ( $\alpha-\beta-$ ) ( $\alpha-\alpha-$ ) ( $\beta-\beta-$ )	75 154 187	1 2 3	} In alcohol.	
Phenanthrene .....	100	1	} In alcohol.	
Anthracene .....	213	2		
Dinitrophenyl ... { (?) 1.4; 1.4	93 213	1 2	} In alcohol.	

### III. INFLUENCE OF ATOMIC ARRANGEMENT ON THE HEATS OF FORMATION AND COMBUSTION.

We may compare the union of two or more atoms in the formation of a compound to the falling of a stone to the earth. The further the stone falls, the greater the amount of heat evolved on its being suddenly stopped; and the nearer the stone gets to the centre of the earth, the greater the attraction between the stone and the earth, and therefore the greater the force required to raise the stone—*i. e.* to separate it from the earth. In an analogous manner, the greater the heat produced in the formation of a compound from its elements, the greater its stability, and the greater therefore the force required to separate the atoms.

Again, if a stone falls halfway towards the earth's centre and afterwards falls the remaining half, then the heat given out at the second half of its journey would be less than in the

† The solubilities of the amides, Ba salts, and Pb salts of the three toluene-sulphonic acids obey the rule as regards the melting-point of the amides, the 1.4 amide, however, melts lower than the 1.2. It therefore seems probable that the orientation of the toluene sulphonic acids is incorrect.



second part of the journey of a stone which had first fallen only one quarter of the way towards the earth and afterwards fell the remaining three quarters. For a stone falling from a given height to the centre of the earth can only produce one given quantity of heat; and if it divides its fall into two parts, then the greater the amount of heat produced at the end of the first portion of its fall the less will be the amount produced in the second part of the fall.

And so it is in the formation of chemical compounds. Suppose we have a compound of carbon and hydrogen; this, on complete combustion, gives out a fixed and definite quantity of heat, say  $3x$ . If now, instead of being completely burnt to carbonic acid and water, the process stops at an intervening point with the formation of two isomeric compounds A and B, and if  $x$  units have been evolved in the formation of A and  $2x$  units in the formation of B, then the heat evolved by the further complete combustion of A and B will be  $2x$  and  $x$  respectively; i. e. of two isomeric compounds, the one which has the greatest heat of formation will have the least heat of combustion, and *vice versa*. We have also seen, that the greater the heat evolved in the formation of a compound from its elements the greater is the attraction between its atoms, and therefore the higher the melting-point. So that, of two isomeric compounds, that which has the highest melting-point will also have the greatest heat of formation and least heat of combustion.

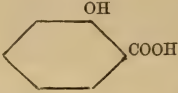
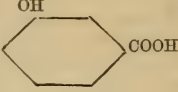

Now though isomeric compounds, as a rule, have *nearly* the same heat of formation, and therefore of combustion, yet they are not exactly the same in this respect. This being so, what is it that causes the difference, small though it may be? The cause can be nothing but the difference in the arrangement of the atoms in the two compounds. And from a comparison of all available data, which in this respect are very meagre, I venture to conclude

(1) *That the stability, and therefore the heat of formation, of symmetrical compounds (and therefore those with highest melting-points) is greater than that of asymmetrical compounds isomeric with them.*

If this be true, it will follow

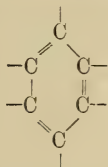
(2) *That the heats of combustion of the former compounds are less than those of the latter.*

The following table contains all the examples to which the above hypothesis can at present be applied:—

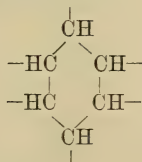
	Formula.	Melting-point.	Heat of formation.	Heat of combustion.
Salicylic acid ..... (1.2)		155	106	759
Methoxybenzoic acid (1.3)		200	111	754
Paraoxybenzoic acid (1.4)		210	115	750
Isopropylene glycol .....	$\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$	?	.....	436
Methylal .....	$\text{CH}_3 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_3$	?	.....	434
Normal propylene glycol ..	$\text{OH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$	?	.....	431
Allyl alcohol .....	$\text{CH}_2 : \text{CH} \cdot \text{CH}_2 \cdot \text{OH}$	?	?	443
Propyl aldehyde .....	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{COH}$	?	69*	426
Acetone .....	$\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3$	?	65	424
Mannite .....	$\text{CH}_2(\text{OH}) \cdot (\text{CH} \cdot \text{OH})_4 \cdot \text{CH}_2(\text{OH})$	166	287	760
Dulcitol .....	?	185	294	753
Methyl formate .....	$\text{H} \cdot \text{COOCH}_3$	Liquid.	.....	252
Acetic acid .....	$\text{CH}_3 \cdot \text{CO} \cdot \text{OH}$	17	.....	210
Ethyl acetate .....	$\text{CH}_3 \cdot \text{CO} \cdot \text{OCH}_2 \cdot \text{CH}_3$	Liquid.	.....	554
Butyric acid .....	$\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix} > \text{CH} - \text{COOH}$	0	.....	497
*Methyl acetate .....	$\text{CH}_3 \cdot \text{CO} \cdot \text{OCH}_3$	.....	.....	395
*Ethyl formate .....	$\text{H} \cdot \text{COOCH}_2 \cdot \text{CH}_3$	.....	.....	391
Methyl valerate .....	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOCH}_3$	.....	.....	856
Ethyl butyrate .....	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOCH}_2 \cdot \text{CH}_3$	.....	.....	823
Amyl acetate .....	$\text{CH}_3 \cdot \text{COOCH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_3$	.....	.....	1036
Ethyl valerate .....	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COO} \cdot \text{CH}_2 \cdot \text{CH}_3$	.....	.....	1019
Normal propyl alcohol ...	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$	.....	.....	480
Isopropyl alcohol .....	$\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_3$	.....	.....	478
Isoamyl alcohol .....	$\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix} > \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$	Liquid.	.....	794
Dimethylethyl carbinol ...	$\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix} > \text{C}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}_3$	12	.....	788
Ethylvinyl carbinol .....	$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH} = \text{CH}_2$	.....	.....	753
Valeraldehyde .....	$\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix} > \text{CH} - \text{CH}_2 - \text{COH}$	.....	.....	742

These relations as regards the heats of formation and combustion of isomeric compounds are thrown out merely as suggestions; for the data are so extremely few in number that I should not be justified in doing more.

I may here mention that Julius Thomsen has shown that the determination of the heat of combustion will in many cases enable us to say whether two or more carbon atoms are united by single, double, or more linkings. Thus, he has shown that ethane is  $\text{CH}_3\text{—CH}_3$ , and propane  $\text{CH}_3\text{.CH}_2\text{.CH}_3$ , *i. e.* that their carbon atoms are united by single links only; whilst in ethylene and propylene two carbon atoms are connected by double linkings, thus,  $\text{CH}_2\text{=CH}_2$ , and  $\text{CH}_2\text{=CH.CH}_3$ ; whereas in acetylene the two carbon atoms are bound by treble linkings,  $\text{CH}\equiv\text{CH}$ . Thomsen also concluded, from the heat of combustion, that the six carbon atoms in benzene are not bound by three double and three single linkings, thus,



but by nine single linkings, thus:—



Bruhl, however, as we shall see presently, concludes from the specific refraction of benzene that the old view is the correct one.

#### IV. INFLUENCE OF ATOMIC ARRANGEMENT ON OPTICAL ROTATION.

According to Pasteur (*Researches*, p. 27), molecules are divisible into two classes:—(1) those in which the atoms are symmetrically arranged, (2) those in which the arrangement is asymmetrical. The property of optical activity belongs to the latter class only; and Le Bel has proposed the hypothesis that when a carbon atom is united directly with four different

elements or radicals, an asymmetrical form of molecule is produced, which must therefore be optically active. This view is supported by Van t'Hoff (*Bull. Soc. Chim.* [2] xxiii. p. 295), who finds, from the comparison of the chemical composition of all known active and many inactive bodies:—(1) *That every organic combination which rotates the plane of polarized light contains an atom of asymmetrical carbon.* The converse of this law, however, does not hold good. This may be attributed either to the presence of two isomerides of opposite rotatory power, or to the fact that asymmetrical carbon is not of itself sufficient to produce optical activity, which may also depend on the nature, as well as on the mutual diversity, of the atoms attached to the asymmetrical carbon atom. The following compounds are all optically active, and all contain an asymmetrical carbon atom, which for distinction is printed in black type:—

Lactic acid .....	$\text{CH}_3.\text{CH}(\text{OH}).\text{COOH}.$ <sup>1</sup>
Malic acid.....	$\text{COOH}.\text{CH}_2.\text{CH}(\text{OH}).\text{COOH}.$
Malamide .....	$(\text{CONH}_2).\text{CH}_2.\text{CH}(\text{OH}).\text{COOH}.$
Aspartic acid .....	$\text{COOH}.\text{CH}_2.\text{CH}(\text{NH}_2).\text{COOH}.$
Asparagine .....	$(\text{CONH}_2).\text{CH}_2.\text{CH}(\text{NH}_2).\text{COOH}.$
Tartaric acid.....	$\text{COOH}.\text{CH}(\text{OH}).\text{CH}(\text{OH}).\text{COOH}.$
Tartaramide .....	$(\text{CONH}_2).\text{CH}(\text{OH}).\text{CH}(\text{OH}).(\text{CONH}_2).$
Secondary butyl carbinol...	$\text{CH}_3.\text{CH}_2.\text{CH}(\text{CH}_3).\text{CH}_2(\text{OH}).$
Methylethylacetic acid ...	$\text{CH}_3.\text{CH}_2.\text{CH}(\text{CH}_3).\text{COOH}.$
Hydroxyglutanic acid .....	$\text{COOH}.\text{CH}_2.\text{CH}_2.\text{CH}(\text{OH}).\text{COOH}.$
Glutamic acid .....	$\text{COOH}.\text{CH}_2.\text{CH}_2.\text{CH}(\text{NH}_2).\text{COOH}.$
Secondary butyl acetic acid.	$\text{CH}_3.\text{CH}_2.\text{CH}(\text{CH}_3).\text{CH}_2.\text{COOH}.$
Mannitol .....	$\text{CH}_2(\text{OH}).(\text{CH}.\text{OH})_4.\text{CH}_2(\text{OH}).$
Glucose.....	$\text{CH}_2(\text{OH}).(\text{CH}.\text{OH})_4.\text{COH}.$
Saccharic acid .....	$\text{COOH}.\text{CH}(\text{OH})_4.\text{COOH}.$
Phenylhydroxyacetic acid..	$\text{C}_6\text{H}_5.\text{CH}(\text{OH}).\text{COOH}.$

(2) *Derivatives of optically active combinations lose their rotatory power when the asymmetry of their carbon atoms disappears. When the contrary happens they do not generally lose it.*

These facts will in the future, no doubt, render great service in determining the constitution of optically active chemical compounds.

# V. INFLUENCE OF ATOMIC ARRANGEMENT ON MOLECULAR REFRACTION.

The molecular refraction of an element  $= \frac{A-1}{d} \times M$ ; where

$A$  = the index of refraction,  $d$  = specific gravity, and  $M$  = molecular weight.

Now Bruhl has recently shown, in a most important series of papers, that the molecular refraction of a compound containing polyatomic atoms is dependent on the manner in which these atoms are combined in the compound, whilst that of monatomic elements is quite independent of this.

The atom of a given element has a definite refractive equivalent, which it retains in all those compounds in which there are no double linkings; so that the refraction-equivalent of such a compound is equal to the sum of the refraction-equivalents of its constituent atoms; consequently, if we know the refraction-equivalents of each of the constituent atoms, we can readily calculate that of the compound. Thus, the refraction-equivalents of the following elements are:—

$$H=1.29; \quad O=2.71; \quad C=4.86;$$

and therefore the refraction-equivalent of alcohol,  $CH_3.CH_2.OH$ , which contains only single linkings, is

$$(2 \times 4.86) + (6 \times 1.29) + 2.71 = 20.17.$$

But we find that, in the case of those compounds containing double linkings between carbon atoms, the observed refraction-equivalent is always in excess of the calculated quantity, as shown in the table, p. 188.

Here we see that, for every double linking of carbon atoms, the refraction-equivalent is raised by two units.

Bruhl has also shown that a similar thing holds good in the case of other polyatomic elements besides carbon. Thus, oxygen, when combined with carbon by a double linking, as in acetic acid,  $CH_3.C=O$ , has a higher refraction-equiva-



lent (3.29) than when combined with only a single link, as in alcohol,  $CH_3.CH_2.OH$ , viz. 2.71.

Monatomic elements, on the other hand, possess refractive equivalents which are constant in all their compounds. The above will show at once what an important influence the double or single linking of atoms has on the refractive equiva-



	Structure.	Formula.	Molecular refraction-equivalent.		Difference.	No. of double linkings $\times 2$ = difference.
			Found.	Calculated.		
Propyl alcohol .	$\text{CH}_3.\text{CH}_2.\text{CH}_2.\text{OH}$	$\text{C}_3\text{H}_8\text{O}$	28.00	27.61	0.39	$\left\{ \begin{array}{l} \text{No double linkings.} \\ = 1 \times 2 = 2 \\ = 2 \times 2 = 4 \\ = 2 \times 2 = 4 \end{array} \right.$
Amylene .....	$\text{CH}_3.\text{CH}_2.\text{CH}_2.\text{CH}=\text{CH}_2$	$\text{C}_5\text{H}_{10}$	39.29	37.20	2.09	
Diallyl .....	$\text{CH}_2=\text{CH}.\text{CH}_2.\text{CH}_2.\text{CH}=\text{CH}_2$	$\text{C}_6\text{H}_{10}$	45.99	42.06	3.93	
Valerylene .....	$\text{CH}_2=\text{CH}.\text{CH}_2.\text{CH}=\text{CH}_2$	$\text{C}_5\text{H}_8$	38.65	34.62	4.03	
Benzene .....	$\left\{ \begin{array}{c} \text{HC}-\text{CH} \\ \diagup \quad \diagdown \\ \text{HC} \quad \text{CH} \\ \diagdown \quad \diagup \\ \text{CH}=\text{CH} \\ \diagup \quad \diagdown \\ \text{HC}-\text{CH} \end{array} \right\}$	$\text{C}_6\text{H}_6$	42.16	36.90	5.26	$= 3 \times 2 = 6$
Toluene .....	$\left\{ \begin{array}{c} \text{HC}-\text{CH} \\ \diagup \quad \diagdown \\ \text{HC} \quad \text{C}-\text{CH}_3 \\ \diagdown \quad \diagup \\ \text{CH}=\text{CH} \end{array} \right\}$	$\text{C}_7\text{H}_8$	50.06	44.34	5.72	$= 3 \times 2 = 6$
Mesitylene .....	$\left\{ \begin{array}{c} \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{C}-\text{C} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C}-\text{CH}_3 \\ \diagdown \quad \diagup \\ \text{C}=\text{CH}_3 \\ \diagup \\ \text{CH}_3 \end{array} \right\}$	$\text{C}_9\text{H}_{12}$	65.22	59.22	6.00	$= 3 \times 2 = 6$

lents of compounds, and also what great service the knowledge of refraction-equivalents is capable of rendering in the determination of the constitution of compounds.

## VI. INFLUENCE OF ATOMIC ARRANGEMENT ON FLUORESCENCE.

Till within a few years ago, the number of bodies known which possessed fluorescing properties was very small. And it is only with the advance of the manufacture of coal-tar colours, and the investigations to which this advance has given rise, that a large number of fluorescing compounds has become known to us; so that the phenomenon of fluorescence has nowadays ceased to be a rarity. Up to the present, however, but little has been done in tracing any connexion between this property and the chemical constitution of the bodies exhibiting it. There can nevertheless be no doubt that it is dependent on a certain grouping of atoms—just as the tinctorial properties are dependent on special atomic groupings, as pointed out by O. N. Witt, to which I shall shortly refer.

Quite recently, Liebermann (*Ber.* xiii. p. 913) has made

an attempt to refer the fluorescent phenomena of the anthracene series to the chemical constitution of the members of this series. According to him, *those derivatives fluoresce in which the two carbon groups binding together the two benzene rings possess the constitution*  $C_6H_4 \begin{smallmatrix} \diagup CM \diagdown \\ | \\ \diagdown CM \diagup \end{smallmatrix} C_6H_4$  (where M = a monatomic element or group); *whilst those derivatives which contain the double ketone group*  $C_6H_4 \begin{smallmatrix} \diagup CO \diagdown \\ | \\ \diagdown CO \diagup \end{smallmatrix} C_6H_4$ , *or the group corresponding to it in phenylanthracene,*  $C_6H_4 \begin{smallmatrix} \diagup C(OH)(C_6H_5) \diagdown \\ | \\ \diagdown CO \diagup \end{smallmatrix} C_6H_4$ , *do not fluoresce.* This rule he finds to hold good in the case of all the 60 to 70 compounds to which it can at present be applied; thus:—

*Fluorescent.*

Anthracene .....	$C_6H_4 \begin{smallmatrix} \diagup CH \diagdown \\   \\ \diagdown CH \diagup \end{smallmatrix} C_6H_4$ .
Dichloranthracene .....	$C_6H_3Cl \begin{smallmatrix} \diagup CH \diagdown \\   \\ \diagdown CH \diagup \end{smallmatrix} C_6H_3Cl$ .
Trichloranthracene .....	$X_1 \begin{smallmatrix} \diagup CH \diagdown \\   \\ \diagdown CH \diagup \end{smallmatrix} X^*$ .
Dibromanthracene .....	„
Tetrachloranthracene .....	„
Anthracene sulphonic acid ...	$C_6H_4 \begin{smallmatrix} \diagup CH \diagdown \\   \\ \diagdown CH \diagup \end{smallmatrix} C_6H_3.SO_3H$ .
$\alpha$ -anthracene disulphonic acid	$X_1 \begin{smallmatrix} \diagup CH \diagdown \\   \\ \diagdown CH \diagup \end{smallmatrix} X^*$ .
$\beta$ -anthracene disulphonic acid &c.	„ &c.

*Non-fluorescent.*

Anthraquinone .....	$C_6H_4 \begin{smallmatrix} \diagup CO \diagdown \\   \\ \diagdown CO \diagup \end{smallmatrix} C_6H_4$ .
Anthraquinone sulphonic acid ...	$C_6H_4 \begin{smallmatrix} \diagup CO \diagdown \\   \\ \diagdown CO \diagup \end{smallmatrix} C_6H_3.SO_3H$ .
Oxyanthraquinone .....	$C_6H_4 \begin{smallmatrix} \diagup CO \diagdown \\   \\ \diagdown CO \diagup \end{smallmatrix} C_6H_3.OH$ .
Alizarine .....	$C_6H_3.OH \begin{smallmatrix} \diagup CO \diagdown \\   \\ \diagdown CO \diagup \end{smallmatrix} C_6H_3.OH$ .
	&c.

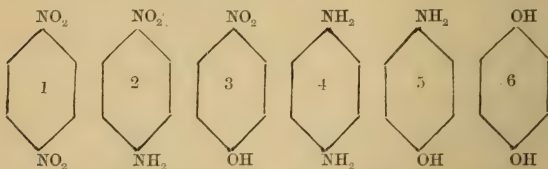
\* Constitution of X and  $X_1$  unknown.

The strength of the fluorescence is very different for different members of the fluorescing series. Thus,  $\beta$ -anthracene disulphonic acid is strongly fluorescent, whilst the  $\alpha$ -acid is but slightly so.

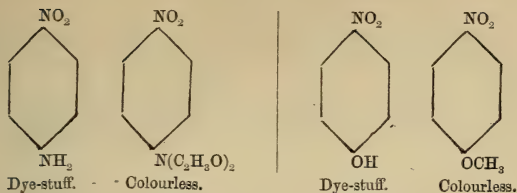
## VII. INFLUENCE OF ATOMIC ARRANGEMENT ON THE TINCTORIAL PROPERTIES.

The influence of chemical constitution on the tinctorial properties of compounds has been studied more especially by Otto Witt (*Ber.* ix. p. 522), whose more important conclusions may be briefly stated as follows :—

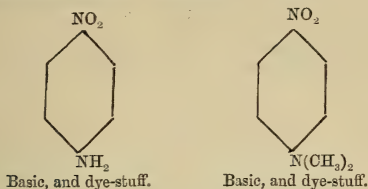
Since benzene is not a dye-stuff, it follows that colouring-properties are conditioned by the side chains. Of the three side chains,  $\text{NO}_2$ ,  $\text{NH}_2$ ,  $\text{OH}$ , not one of them alone is capable of producing a compound possessing tinctorial properties; for  $\text{C}_6\text{H}_5.\text{NO}_2$ ,  $\text{C}_6\text{H}_5.\text{NH}_2$ ,  $\text{C}_6\text{H}_5.\text{OH}$  are all colourless bodies. It is possible, however, that certain combinations of two or more of these groups will produce the necessary result; thus, of the six possible compounds,



only 2 and 3 are dye-stuffs. We therefore see that the combination of the nitro-group with the amido-, or hydroxyl groups, produces a colouring compound; or, in other words, the presence of a  $\text{NO}_2$  and a salt-forming group conditions the dyeing properties. The nitro-derivatives of benzene are to a certain extent coloured; but it is only on the introduction of a salt-forming radical that we get a true dye-stuff. That to obtain a dye-stuff the presence of a  $\text{NO}_2$  group and a salt-forming radical is necessary, is shown by the fact that if we destroy the basicity of an amido-group by the introduction of an acetyl group, or if we destroy the acidity of a hydroxyl group by introducing a methyl group, the compound entirely loses its colouring-properties, though by these changes no alteration has been produced in the general constitution of the compound. Thus



If, however, we methylate the  $\text{NH}_2$  group of nitro-aniline, we do not destroy its tinctorial properties, because we do not at the same time destroy its basicity. Thus



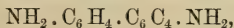
From such considerations as these Witt has enunciated the following laws:—

(1) *The tinctorial properties of aromatic compounds are conditioned by the simultaneous presence of a colour-imparting group (such as a nitro-group) and of a salt-forming group (such as  $\text{NH}_2$  or  $\text{OH}$  group).*

The colouring group he terms the *chromophor*; and a compound containing a chromophor, and in which a salt-forming radical is still wanting for the formation of a dye-stuff, he calls a *chromogen*: thus  $\text{NO}_2$  is the chromophor of  $\text{C}_6\text{H}_4\cdot\text{NO}_2\cdot\text{NH}_2$  and  $\text{C}_6\text{H}_4\cdot\text{NO}_2\cdot\text{OH}$ , whilst  $\text{C}_6\text{H}_5\cdot\text{NO}_2$  is the chromogen of both compounds.

Further, the tinctorial properties increase with the number of  $\text{NO}_2$  groups present; thus, the nitrodiphenylamines are all acids and dye-stuffs, and their dyeing-power increases with the number of  $\text{NO}_2$  groups.

Again, azobenzene,  $\text{C}_6\text{H}_5\cdot\text{N}=\text{N}\cdot\text{C}_6\text{H}_5$ , though of a dark yellow colour, is not a dye-stuff; nor is benzidine,



though it is a strong base; but as soon as we combine the properties of the two, by introducing into the latter compound the chromophor  $-\text{N}=\text{N}-$ , or a salt-forming group into the former, we get a series of beautiful dye-stuffs.

Another point observed by Witt is

(2) *The chromophor exerts its tinctorial influence much more in the SALTS of a dye-stuff than when the latter is in the free state.*

Thus, nitraniline, nitrophenol, and picric acid, when pure, are pale yellow, whilst their salts are dark orange and sometimes red.

Again,

(3) *Of two dye-stuffs, both possessing in other respects a similar constitution, that has the highest tinctorial power whose salts are the most stable.*

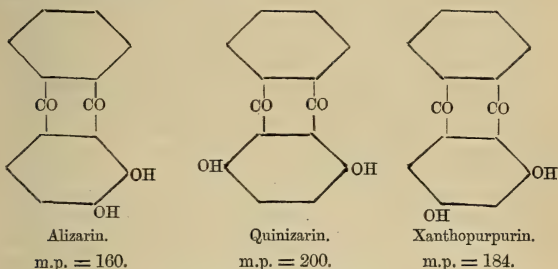
Since most dye-stuffs owe their basicity or acidity to the presence of the  $\text{NH}_2$  or  $\text{OH}$  group, each chromogen may give rise to two colouring compounds. All dye-stuffs, therefore, may be arranged in pairs; and it is worthy of notice that corresponding dye-stuffs always have a similar colour. Thus,

Nitrophenol .....	$\text{C}_6\text{H}_4\cdot\text{NO}_2\cdot\text{OH}$	} bright yellow.
Nitroaniline .....	$\text{C}_6\text{H}_4\cdot\text{NO}_2\cdot\text{NH}_2$	
Picric acid .....	$\text{C}_6\text{H}_2\cdot(\text{NO}_2)_3\cdot\text{OH}$	} dark yellow.
Trinitraniline ...	$\text{C}_6\text{H}_2\cdot(\text{NO}_2)_3\cdot\text{NH}_2$	
Amidoazobenzene	$\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}=\text{N}\cdot\text{C}_6\text{H}_5$	} yellow.
Oxyazobenzene...	$\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}=\text{N}\cdot\text{C}_6\text{H}_5$	
Tetramidotetrazotriphenyl .....		} brown.
Tetroxytetrazotriphenyl .....		
Rosaniline .....		} red.
Rosolic acid .....		
Dioxyanthraquinone or alizarin .....		} red or violet.
Diamidoanthraquinone .....		

All the compounds referred to above (except the two anthraquinone derivatives) contain a nitrogenous chromophor. The dye-stuffs of anthraquinone, however, show that a carbon group may be a chromophor. Neither anthraquinone nor dioxyanthracene are dye-stuffs; whilst a combination of both, viz. alizarin or dioxyanthraquinone, is a powerful colouring agent. The double ( $-\text{CO}-$ ) group is therefore the chromophor of alizarin and the related dye-stuffs. These compounds also lose their colouring-properties on the introduction of methyl into the hydroxyl groups. If we increase the salt-forming power of alizarin by introducing more hydroxyl groups, or by nitration or amidation, we also increase the tinctorial properties. Further, in alizarin and the related



dye-stuffs, one of the hydroxyl groups must be in the ortho-position as regards the ( $\text{—CO—}$ ) group in order that the compound may be a dye-stuff. For there are numerous isomers of alizarin, but most of them are colourless, only quinizarin and xanthopurpurin possessing tinctorial properties; and in these, as well as in alizarin, one of the HO groups is in the ortho-position, thus:—



In the above sketch I have endeavoured to give a brief account of the more important facts which have come to light during late years in reference to the influence of chemical constitution on the physical properties of organic compounds.

I had intended saying something of this influence of atomic arrangement on the specific volume of compounds and also on the chemical activity, or the susceptibility of certain elements or groups of elements in a compound being replaced by other elements or groups of elements; but my remarks have already attained more than sufficient length, and to do these latter subjects full justice would require the space of another paper.

XXII. *Apparatus for calculating Efficiency.* By C. VERNON BOYS, A.R.S.M., *Demonstrator of Physics at the Normal School of Science, South Kensington*\*.

[Plate V.].

IN a previous paper I have shown how work done in an engine or transmitted by shafting or belting, or expended by an electric current, or how the quantity of electricity which has passed in a conductor during any time, may be automatically measured and integrated or recorded. The present paper refers to apparatus for dividing rates of growth

\* Communicated by the Physical Society, having been read at the Meeting on January 28, 1882.

of two integrals so found one by the other, and continuously recording the quotient. Before describing any of these machines, it may be well to give an example showing an application of a divider to some useful purpose. Let there be a steam-engine driving a dynamo-electric machine, which is employed to produce an electric light. Steam does work on the piston of the engine, which may be integrated as already described. This is the work put in. The electricity does work in the electric arc and in the conducting wires, which may be integrated. This is the work taken out. If after any time, say one hour, the work taken out is divided by the work put in, the quotient will represent the average efficiency of the engine and machine combined during the hour. In like manner, if the readings are taken after a minute, the quotient will give the average efficiency during the minute. If instead of a minute an indefinitely short period of time is occupied, then the quotient obtained will give the true efficiency *at* that time. Now, if by mechanism or otherwise a curve can be drawn in which the ordinates represent the true efficiency, while the abscissæ are time, then an inspection of the curve will show exactly how well the machines have done their work at every moment, and the highest points will indicate the time at which the best results have been obtained. What is wanted in practice is not a curve giving the true efficiency as above described, because work is not put into an engine uniformly, but intermittently, but a curve showing the average efficiency for the last few seconds or minutes as the case may be; and it is this that the mechanism I am going to describe accomplishes. If one of the integrals represents time, and the other work done in an engine, then the curve gives the continuous value of the horse-power per hour; or if one integral represents turns of a dynamo-machine, while the other represents electric current or electric energy, then the curve gives current-quantity or current-energy per turn. Or, generally, if two things are turning, either or both at a variable rate, a dividing machine will give the ever-varying value of the quotient of one by the other.

I have made use of two principles in the construction of dividing machines, which may therefore be classed under two heads. In the first class a pointer, if at a wrong position on the scale of quotients, moves towards its right place with a speed proportional to its distance from it: its motion is therefore of a logarithmic nature. In machines of the second class a pointer, if at a wrong position on the scale of quotients, changes its speed of moving towards its right position with a speed proportional to its distance from it: its motion therefore is of an harmonic nature. In either case the movement of the

pointer may be made to trace a diagram on a travelling band of paper. I shall describe one logarithmic, and three harmonic dividers.

*Logarithmic Divider.*

For this a pair of wheels incapable of steering are required—that is, wheels which when turned while their edges are in contact with a surface are compelled to move forward, but which at the same time are perfectly free to move laterally. Disks with smoothly milled edges very imperfectly fulfil these conditions; but an outside smoke-ring, such as is described in the smoke-ring integrator on p. 79, *Phil. Mag.* Feb. 1882, should answer this purpose well. Let two such smoke-rings be mounted on a common axis, but so that each may revolve independently of the other; let there be a disk so supported that its plane is parallel to the common axis, and so that its own axis would if continued meet the other at a point midway between the two smoke-rings; moreover, let the axis of the disk be carried by an arm in such a manner that it is capable of moving in a direction parallel to the plane of the disk, but inclined at a small angle to the common axis of the smoke-rings. Fig. 1 shows the arrangement in its central position:  $AA$  is the common axis,  $SS_1$  are the smoke-rings, and  $D$  the disk; the dotted line shows the line of travel of the axis of the disk. If while the disk is in its central position the two rings  $SS_1$  are caused to revolve at equal speeds in opposite directions, then the disk merely turns, and there is no further result. Let the direction of motion be that shown by the arrow.

Now let the ring  $S_1$  begin to revolve faster than  $S$ , then the centre of the disk  $D$  would, if free, begin to move downwards with a speed equal to half the excess; but it is incapable of moving vertically downwards; yet it may move down the slope indicated by the dotted line. Now, as the rings  $SS_1$  in no way interfere with the lateral movement of the disk, its centre will move down the slope till it reaches such a point that the ratio of the distances of the point from the two rings is equal to the ratio of the speeds. It will be necessary to show that what is true when the produced axis of  $D$  intersects  $AA$ , is equally true when it has so far moved up or down the slope as to cause a considerable displacement. Let the centre have moved down to  $c$ , fig. 2, and let  $SS_1$  be the points on the disk touched by the two smoke-rings, and let  $cp$  be the perpendicular on  $SS_1$  from  $c$ . Now, if  $SS_1$  are turning with speeds proportional to the lengths  $Sp$  and  $S_1p$ , then the centre will have no tendency to move up or down. The motion of  $S$  about  $c$  as a centre may be resolved into two:—one, an upward motion, proportional to  $Sp$  (and this motion

must, from the mechanical construction, be the same in the disk and in the ring); and the other, a lateral motion, proportional to  $pc$ , with which the ring in no way interferes. In a similar way, the motion of  $S_1$  may be resolved into two—a downward motion proportional to  $S_1p$ , and a lateral motion proportional to  $pc$ . The downward motion must be common to the disk and ring, while the lateral motion is free. It is clear then, if the rings move with speeds in the ratio  $S_p : S_1p$ , that the centre  $c$  will have no up or down tendency; and if the rings are not moving with speeds in the ratio  $S_p : S_1p$ , that the centre  $c$  will move up or down the slope with a vertical speed proportional to the distance of the point  $p$  from a point which does divide  $SS_1$  in the ratio of the speeds of the smoke-rings. If  $\theta$  is the inclination of the dotted line, then  $c$  will move along this line with a speed equal to  $\text{cosec } \theta$  times its vertical speed, and  $p$  will travel along  $SS_1$  with a speed equal to  $\cot \theta$  times the vertical speed of  $c$ . Should one disk ever stop and change the direction of its motion, then  $c$  must move along the slope till it is immediately under the ring, and move beyond till it arrives at such a position  $c_1$  that  $S_{p_1} : S_1p_1$  is the ratio of the speeds.

Let the two smoke-rings be turned by two integrating machines as already described, then either or both may be going at a variable speed. There must at every moment be some point  $x$  in the line  $SS_1$  such that  $Sx : S_1x$  is the ratio of the speeds. This point will sometimes coincide with  $P$ , at which times  $C$  will be stationary; it will generally, however, be distant more or less from  $P$ , in which case  $P$  will pursue it with a speed proportional to its distance from it. If the arm which carries  $C$  carries also a pencil bearing against a uniformly travelling band of paper, then the curved line drawn will show what has been the efficiency, horse-power per hour, or whatever it was set to find during any period of time. The travelling band would have to be ruled across with lines showing time, and longitudinally with lines showing ratios, the scale being of the kind shown in fig. 3.

If the slope or the direction of motion had been in the opposite direction to that shown, then  $p$ , instead of approaching its places, would have fled from it with a speed proportional to its distance from it.

I think it possible that the logarithmic divider might be applied to solve some difficult problems; for while in action the inclination of the path of the centre  $c$  to the line  $SS_1$ , or the position of either ring on their common axis, may be changed in any way without interfering with the freedom of the motion of  $c$ .

*Harmonic Dividers.*

All harmonic dividers depend on the steering-power of wheels, an action which renders wheels of ordinary construction useless in the case of the logarithmic divider. The steering action, however, is not determined by any direct effect, as in the case of my cart integrating-machine, or in the more familiar case of a common bicycle, but depends on an intermediate action, and is in this respect exactly similar to the steering arrangements in that most beautiful and ingenious machine the "Otto" bicycle. In this the rider produces a difference in the speeds of two wheels, one on each side of him; the angular deviation therefore is the integral of the difference in speed between the two wheels, while the linear deviation from the original straight course is the integral with respect to the distance run of the sine of the angular deviation. The method of adapting this principle is exactly analogous to the case of the disk-cylinder integrator. That machine was developed in this way:—Take a cart integrator running on fixed ground, remove the whole of the cart except its steering-wheel, which fix in position, then give it movable and cylindrical ground to run on; a disk-cylinder integrator will be the result. In this case do away with the whole of Otto's machine except the two wheels, fix them in position, and give them each a movable floor to run on. Fig. 4 is a side view, and fig. 5 is a plan, of a machine of this kind.  $A A_1$  are the two steering wheels mounted independently on a common axis;  $B B_1$  are a pair of disks geared together by their edges, and they form the movable floors for the disks  $A A$  to rest upon.  $c c_1$  are the supporting wheels of a frame  $F$ , and are capable of running on rails parallel to the common axis of  $A A_1$ . The frame  $F$  carries a block  $D$  swivelled on a vertical axis passing through the centre of both  $F$  and  $D$ . The axes of  $B B_1$  are supported by  $D$ . If  $A A_1$  are caused to turn with speeds proportional to their distances from the centres of  $B B_1$  and in the same direction,  $B B_1$  will revolve at equal speeds in opposite directions, and neither  $D$  nor  $F$  will be affected; but if either  $A$  or  $A_1$  is made to revolve a little faster than is due to its central distance,  $D$  will begin to turn in its swivel-frame. But no sooner does  $D$  begin to twist, than the disks  $A A_1$ , which previously were describing circles on  $B B_1$ , tend to move in spiral paths, the faster one receding from, and the slower one approaching, the centres of the disks  $B B_1$  on which it is moving. But as  $A A_1$  are incapable of any movement but rotation, while the disks  $B B_1$  can, from the nature of their support, accommodate themselves to every kind of movement



except one of lateral translation, therefore the combination  $c$ ,  $F$ ,  $D$ ,  $B$ , and  $B_1$  will move longitudinally till the central distances of  $A$   $A_1$  are proportional to their speeds; but, unfortunately, by this time the obliquity of the block  $D$  has become a maximum, and therefore its rate of longitudinal travel is a maximum also. It therefore travels on and introduces an error of position on the opposite side, which is corrected as before; and so the frame  $F$  oscillates on either side of its correct position. The motion may be considered more exactly in this way:—The rate at which  $D$  twists is proportional to the error of  $F$ , while the rate at which  $F$  corrects its position is proportional to the amount of twist of  $D$ : this expressed mathematically gives the equation  $\frac{d^2y}{dx^2} = -y$ , the solution of which is  $y = \sin x$  or  $y = \cos x$ . The motion of both  $D$  and  $F$  therefore is harmonic. An exactly analogous case is that of a heavy body moving under the influence of a force which varies with the displacement, the movements of  $F$  being equivalent to that of the heavy body, while the rate at which  $D$  twists represents the force. Of course in the dividing-machine described we have nothing to do with inertia or with a resisting force; but the movements are the result of an action of pure rolling, and it so happens that they follow exactly the same law as the movements of a vibrating heavy body. This view of the subject removes all difficulty in discovering what will be the action during either slow or very rapid variations in the ratio of the velocities. Let the dynamical equivalent be a heavy magnetic needle balanced in a magnetic field. Then the direction of the field corresponds to ratio of velocities, and the motions of the needle to the motion of the frame  $F$ . As has been shown in the case of a constant ratio, an error of position of  $F$  at starting causes  $F$  to oscillate on either side of its correct place, just as a displacement of a magnetic needle causes it to oscillate. Now suppose  $F$  to be in its correct position and then the ratio to change slowly (that is, slowly compared with the time of an oscillation); then the frame  $F$  will move slowly also, always being in the correct position, because during a slow change in the direction of the magnetic field a balanced needle follows the change without oscillation. Next suppose the ratio to alternate rapidly—that is, rapidly compared with the time of an oscillation, as, for instance, is the case when a steam-engine is made to do work uniformly, for work is put in intermittently and taken out gradually; then the dividing-machine will steadily show the mean value, and will take no account of the rapid variations

in ratio, because a heavy magnetic needle subjected to rapidly alternating currents, which produce rapid variations in the direction of the magnetic field, is unaffected by these currents, but steadily maintains its position in the mean direction of the field. The most complex possible case is a combination of rapidly alternating and slowly changing ratios with occasional sudden changes. The first two are properly considered by the machine, while the sudden changes merely cause the frame  $F$  to oscillate on either side of its correct position. As in the case of the logarithmic divider, so here; a curve may be drawn on a travelling band of paper by a pencil attached to the frame.

A more simple arrangement is shown in fig. 6, where the disks  $B B_1$  and the frame and block are replaced by a sphere  $S$  with its axis horizontal mounted in a horizontal ring  $R$ , and where this ring is supported in a crutch  $c$  which is capable of moving round on a vertical axis. Thus, when  $R$  is horizontal, the sphere can turn independently round three axes at right angles to one another. Then, if the disks  $A A_1$  touch the sphere in points  $90^\circ$  apart, the ratio of their speeds will be measured by the tangent of the inclination of  $R$ , while the deviation of  $c$  will correspond to the obliquity of the block  $D$  in the last machine.

The most simple harmonic divider that I can imagine is made by mounting, as shown in fig. 7, two iron cones with their bases adjacent, and with the lowest generating line in each horizontal and in one straight line. Then, if a magnetized steel reel is hung on and the two cones are turned, the reel will travel about and find the ever-varying value of the ratio of their speeds. The method of attaching a recording-pencil is too obvious to need description. If the two cones were placed so that their bases were turned away from one another instead of being adjacent, then the reel would change its speed of moving *away* from its correct position with a speed proportional to its distance from it. This kind of action could only exist, of course, for a very short time.

Whether dividing-machines are likely to be of general value for practical or experimental purposes, it is difficult to say; but there can be little doubt that cases might arise in which some machine such as I have described might be used with advantage.

XXIII. *On the Electrical Resistance of Gases.* By E. EDLUND,  
*Professor of Physics at the Swedish Royal Academy of  
 Sciences\*.*

§ 1.

THE resistance opposed by gases to the propagation of electricity has shown itself to be different in several respects from that produced by solid or liquid conductors. I shall in this memoir take these differences into consideration, and endeavour to show how they are to be explained.

1st. In order that the current may traverse a solid or liquid conductor, there is no need of a certain amount of electromotive force. However slight the electromotive force may be, the current will nevertheless pass, although of course it becomes less intense as the force is diminished or the resistance increased. Only when the force is equal to *nil* will the current become equal to *nil*. With gases, on the contrary, the circumstances change. For the current to be able to traverse a gas the source of electricity must have a certain amount of electromotive force, or be capable of producing a certain electrical tension, the amount of which depends moreover on the chemical nature, the density, and the temperature of the gas, but never falls below a certain limit in given circumstances. For any electromotive force below that limit the gas is a perfect insulator.

2ndly. The quantity of heat produced by an electric current in its passage through a solid or liquid conductor is, as is known, proportional to the square of the intensity of the current. In gases, on the contrary, the amount of heat is proportional to the first power of the intensity of the current, and not to its square. This remarkable property of gases was first observed by G. Wiedemann†; and later it was completely demonstrated by Naccari and Bellati that the quantity of heat evolved is really proportional to the quantity of electricity which has passed‡.

3rdly. For solid and liquid conductors the quantity of heat developed, under conditions in all other respects equal, by a given current, is inversely proportional to the cross section of the conductor; while the quantity of heat developed in a column of gas is independent of the section of the latter. This proposition has in like manner been demonstrated experimentally by G. Wiedemann, as well as by Naccari and Bellati.

4thly. In a solid or liquid conductor the resistance is in-

\* Translated from a copy, communicated by the Author, of the memoir forming No. 7, vol. vi. of the *Bihang till K. Svenska Vet.-Akad. Handlingar*.

† Pogg. Ann. cxlv. p. 237.

‡ Beiblätter zu den Ann. der Ph. und Ch. ii. p. 720 (1878).

versely proportional to the section of the conductor. G. Wiedemann has proved, by experiments \*, that the tension which is necessary upon the electrodes in order to force the electricity of a Holtz machine to traverse a cylindrical tube filled with rarefied gas is independent of the radius of the tube—which means, in other terms, that the electrical resistance of the gas is independent of the section of the tube. In two experiments, one with a tube 16 millim. and the other with a tube 0·5 millim. in diameter, Schulz† found only an insignificant difference in the electrical tension requisite to compel the electricity of a Holtz machine to pass through the tube.

5thly. With solid and liquid conductors, the difference between the electroscopic tensions on two points situated at a certain distance the one from the other is proportional to the product of the resistance between those points multiplied by the intensity of the current. Warren De la Rue and Hugo Müller‡, have, on the contrary, proved experimentally that the difference between the electroscopic tensions at two points situated at a distance from one another in a column of gas is totally independent of the intensity of the current. These physicists caused the current of a battery composed of a great number of elements to vary between very wide limits; and yet it was impossible to perceive any variation in the above-mentioned difference. With the aid of a galvanic battery of great electromotive force, Hittorf has also proved, although in another way, that the difference between the electric tensions of the electrodes conducting to the column of gas is independent of the intensity of the current§. When for the column of gas between the electrodes a liquid conductor was substituted, the difference became, as might have been expected, proportional to the intensity of the current. From this Hittorf draws the conclusion, somewhat prematurely, that the resistance of the column of gas must be in the inverse proportion of the intensity of the current, to which circumstance he attributes a fundamental importance for the conductivity of gases.

6thly. Several years since, Edm. Becquerel proved||, by experiments, that gases begin to be conductors when heated to the temperature of redness, after which their conductivity increases in proportion as the temperature rises above that point. If the temperature is sufficiently elevated, they even let the feeble current of a single element pass. The conducti-

\* Pogg. *Ann.* clviii. p. 53 (1876). † *Ibid.* cxxxv. p. 254 (1868).

‡ *Comptes Rendus*, lxxvi. p. 1072 (1878).

§ Wied. *Ann.* vii. p. 573 (1879).

|| *Ann. de Ch. et de Ph.* [3] xxxix. p. 377 (1853).

vity moreover increases as the density of the gas diminishes. The fact that gases heated to redness become conductors was at first questioned, although erroneously, by Beetz\* and G. Wiedemann†, but has since been confirmed in the most complete manner by Hittorf‡.

But Becquerel's experiment has furnished another result, to which I will call special attention. When, keeping the same battery, the intensity of the current was modified by introducing a rheostat of greater or less resistance, the resistance of the gas was shown to be dependent on the intensity of the current. For example,  $i$  and  $i_1$  designating the current-intensities, let  $E$  be the electromotive force,  $r$  and  $r_1$  the resistances of the solid or liquid conductor,  $z$  and  $z_1$  the gas resistances, corresponding to  $i$  and  $i_1$ , we get, according to Ohm's formula,  $i = \frac{E}{r+z}$  and  $i_1 = \frac{E}{r_1+z_1}$ . When the current does not pass through the gas, and  $M$  and  $M_1$  designate the resistances necessary in order that the current-intensities may become the same as before, we shall have  $i = \frac{E}{M}$  and  $i_1 = \frac{E}{M_1}$ , whence we get  $M - r = z$  and  $M_1 - r_1 = z_1$ . Putting the calculation thus, it will be seen that the resistance of the gas was nearly proportional inversely to the intensity of the current which had passed.

The observation numbers obtained also appear to indicate that the resistance of the gas increases with the number of the elements of the battery employed, although the intensity of the current be maintained constant by introducing a suitable rheostatic resistance. We will not now dwell upon this almost incomprehensible result (as Becquerel himself remarks), seeing that W. De La Rue and H. W. Müller§ have quite recently found, in their investigations, which, however, were executed by other processes than those of Becquerel, that the resistance of gases at one and the same current-intensity is independent of the number of the elements.

The above-mentioned differences between solid and liquid conductors, on the one hand, and gases on the other, are explained without difficulty if the unitarian theory of the nature of electricity explained by me|| be taken as the starting-point. In order, however, to furnish the proof of what I advance, it is necessary first to cite some propositions of that theory.

\* *Fortschritte der Physik*, ix. p. 479 (1853).

† *Die Lehre vom Galvanismus*, 2nd ed. vol. i. p. 339.

‡ *Pogg. Ann.* Jubelband, p. 234 (1874).

§ *Phil. Trans.* clxix. p. 236 (1878).

|| *Théorie des Phénomènes Electriques*, Mem. Roy. Ac. Sciences, Sweden, vol. xii. no. 8 (1874).



## § 2.

(a) According to the unitarian theory, the galvanic current in a closed circuit consists in the free æther present in the circuit being set in translatory motion. The intensity of the current is determined by the quantity of æther passing, in the unit of time, through any section of the conductor; and the velocity of the æther, for equal intensity of current, is inversely proportional to the magnitude of the section. The galvanic current may therefore be compared to the current of an ordinary gas in a system of tubes; and the properties belonging to a current of this latter kind are therefore to be met with, *mutatis mutandis*, in the æther-current. Thus, let us imagine a tube, of which one half has the section 1, and the section of the other half is  $n$  times as great; let us suppose, secondly, that this tube is filled with a fluid (liquid or gaseous) having a translatory motion impressed by forces acting at one of the extremities of the tube. Now, if we wish to stop or diminish at any point the motion of the fluid by a counterpressure (for instance, by means of a piston or otherwise), in order to attain *the same effect* we must cause to act in the widest part of the tube  $n$  times as much pressure as in the narrowest. The diminution of the velocity of the motion by means of the counterpressure does not depend on the absolute value of the latter, but on its value in comparison with the unit of section. If the counterpressure upon the unit of section is as strong in the widest part of the tube as in the narrowest, the diminution of the intensity of the current is equal in the two cases. It will always be so, whatever the resistance, provided that the fluid employed possess sufficient fluidity to produce equal pressure in all directions.

What has just been said finds its direct application in the galvanic current. Whatever opinion may be held upon the nature of electricity, all agree that it is a fluid which the extreme mobility of its particles permits to communicate pressure in all directions. Galvanic resistance impedes the motion of electricity; it therefore acts as a pressure in the opposite direction distributed uniformly over all points of the section of the conductor. Now, if two resistances (two wires, for instance, each of a different metal, and with different sections) produce an equal diminution in the intensity of a given current, their resistance is said to be equal. We know, likewise, in conformity with the foregoing, that the counterpressure opposed by each of them, on the unit of section, to the propagation of the current is in like manner equal. It is therefore exclusively the counterpressure on the unit of section that can serve for the determination of the galvanic resistance. This

is a consequence of the laws of hydrodynamics; and it is impossible to give any other interpretation to the fact if we will continue to admit that the electric material is a fluid.

Now let us suppose a single conducting wire or a liquid column  $f$ , of which the section is 1, and also a number  $n$  of other conductors,  $f_0, f_1, f_2$ , &c., of the same material, section, and length as the preceding, placed side by side. Let us then suppose that a current  $i$  passes through the conductor  $f$  and afterwards simultaneously through the conductors  $f_0, f_1, f_2$ , &c. placed side by side. Each of these latter will therefore have to be traversed by a current  $= \frac{1}{n} i$ . Now we know by experiment that the resistance to be overcome by the current in order to pass simultaneously through the  $n$  conductors  $f_0, f_1, f_2$ , &c. constitutes  $\frac{1}{n}$  of the resistance to be overcome when the current passes through  $f$ . According to the above account, the counterpressure upon the unit of section of the  $n$  conductors will be likewise  $\frac{1}{n}$  of the counterpressure in the single conductor  $f$ , the resistance being determined exclusively by the amount of the counterpressure upon the unit of section. It hence follows, therefore, that in each of the conductors  $f_0, f_1, f_2$ , &c. the resistance will in the present case be  $\frac{1}{n}$  of what it is in  $f$ . We therefore find ourselves confronted by the unexpected result that *galvanic resistance is proportional to the intensity of the current*. It must, however, be observed that this demonstration refers only to solid and liquid, and not at all to gaseous bodies, to which the above experiment is not applicable.

The above-mentioned result is in direct opposition to the opinion hitherto generally admitted, namely that the resistance is independent of the intensity of the current. But if that opinion is still to be maintained, it will be necessary, in consequence of the foregoing, to assume that the fluid which we call electricity is governed by quite different laws of motion from those to which the other fluids known to us are subject. It has moreover been demonstrated in the above-mentioned memoir, that although the formulated proposition may contradict the common opinion, it is by no means contrary to the experimental results upon which that opinion has been believed to be founded.

In consequence of the results of experiment, as also from the theoretical consideration above given, we have, then, as

the expression of the resistance  $r_0$  in a conductor of length 1 and section  $a$ , traversed by the current  $i$ ,

$$r_0 = \frac{ki}{a} = ri,$$

where  $k$  is a constant dependent on the chemical and physical nature of the conductor, as well as on the temperature. The constant  $k$  is evidently the resistance in a conductor of section 1 and length 1, passed through by the current 1;  $\frac{i}{a}$  is the intensity of the current on the unit of section;  $r$ , or, in other terms, what we have hitherto named the galvanic resistance, is nothing else but the resistance per unit of intensity of the current. In order to distinguish this resistance from the others, in the following we call it the principal resistance.

(b) Electromotive force, like all other motive forces, is measured by the acceleration which it can impart, in the unit of time, to the unit of mass. Taking this for granted, which we are warranted in doing under all the circumstances, Ohm's law can be without difficulty deduced from ordinary mechanical principles. We will nevertheless previously show that the electromotive force is independent of the intensity of the current.

Electromotive force acts with equal intensity upon every point of the electromotive surface of contact; consequently the total value of this force increases proportionally to the extent of that surface. Besides, it is evident that the force not only acts upon the æther molecules which are at the contact surface itself, but also extends to those situated at a very little distance from that surface. Now let us designate by  $E$  the quantity of motion which the electromotive force can communicate to the mass of æther on each unit of surface in the unit of time. Let us, in the first place, imagine a current sufficiently powerful for the unit of mass to pass, in the unit of time, through each unit of the surface of contact; then each unit of mass will have received the acceleration  $E$ . If the extent of the surface of contact be called  $n$ ,  $nE$  will in this case constitute the total value of the electromotive force. Let us suppose, secondly, the surface of contact passed through, in unit of time, by a mass of æther  $p$  times as great as before, and which can then be expressed by  $pn$ . The æther possessing the same density in a feeble as in an intense current, the velocity will in this case be  $p$  times as great. Each particle of the mass of æther therefore undergoes the action of the electromotive force during a space of time constituting  $\frac{1}{p}$  of the time

of action in the former case. The acceleration acquired amounts to only  $\frac{E}{p}$ . On multiplying by the mass  $pn$ , we shall have the total electromotive force equal to  $nE$ . Thus the electromotive force can be expressed by  $nE$ , whether the current be strong or weak.

If  $r$  signifies the totality of the principal resistance, and if  $i$  designates the intensity of the current, the total resistance will be  $ri$ —which in this case signifies nothing else but the counterpressure, upon the unit of section, opposed by the resistance to the propagation of the current. We shall therefore have  $nri$  for the total value of the counterpressure upon a surface of contact of  $n$  units magnitude. Designating by  $L$  the total length of the circuit, we thus obtain the equation of motion,

$$L \frac{di}{dt} = nE - nri^*,$$

whence

$$i = \frac{E}{r} \left( 1 - e^{-\frac{nrt}{L}} \right).$$

As soon as the current has become constant we have

$$i = \frac{E}{r}.$$

It follows from this that the electromotive force represented in Ohm's formula is independent of the extent of surface of the electromotor—which, we know, is conformable to experience.

(c) Let us imagine a closed galvanic conductor, of which the length is  $l$  and the section everywhere equal to  $a$ , composed of the same material throughout its length, and passed through by a constant current of intensity  $i$ . If  $\delta$  is the mass of æther in motion per unit of volume, and  $h$  the velocity of the motion, we shall have  $i = a\delta h$ . To calculate the mechanical work done by the current during the unit of time, we shall first consider a current-element comprised between two

\* The total length  $L$  of the circuit being equal to the sum of all its parts  $l_1, l_2, l_3, l_4$ , &c., and these having respectively the sections  $a_1, a_2, a_3, a_4$ , &c., the total volume of the conductor will be  $a_1 l_1 + a_2 l_2 + a_3 l_3 + \&c.$  By multiplying this sum by the mass of æther  $\delta$  in the unit of volume, we obtain the entire mass of the æther in motion. Now, if the augmentation of the velocity during the time  $dt$  is respectively  $dh_1, dh_2, dh_3$ , the total mass of æther will receive, during the time in question, an augmentation of the quantity of motion which will be expressed by  $(a_1 l_1 dh_1 + a_2 l_2 dh_2 + a_3 l_3 dh_3 + \dots) \delta$ . Now  $\delta a_1 \delta h_1 = \delta a_2 \delta h_2 = \delta a_3 \delta h_3 = \delta i$ , whence, consequently, the total augmentation of the quantity of motion of the æther will be  $L \delta i$ .

planes situated at distance 1 from each other. The resistance upon the unit of section being  $r_0$ , and the magnitude of the section  $a$ , the resistance upon the entire section will be  $r_0 a = ki$ . In the time-unit this element is repelled the path-length  $h$ , whence the work done will be  $kih$ . Now  $h = \frac{i}{\delta a}$ , in which expression  $\delta$  is a constant, as we have seen above. The mechanical work of this element will therefore be  $\frac{ki^2}{\delta a}$ . If this quantity be multiplied by  $b$ , the product  $\frac{kli^2}{\delta a}$  will be equal to the work of the entire current. If, lastly, this expression be multiplied by the thermal equivalent of the unit of work, and if the constant  $\delta$  be made to enter into  $k$ , the quantity of heat produced by the current during the time-unit will be equal to  $\frac{Akli^2}{a}$ , which is known to be in accordance with experiment.

The calculation can be effected with equal facility, on the same principles, in the case in which the section and the nature of the conductor vary from one part to another.

(d) With respect to the production and distribution of free æther at the surface of a galvanic conductor, these can best be explained in the following manner:—

Let us imagine a tube in which a mass of gas is set in motion by a force acting at one extremity, while the gas can issue freely at the other. Let us assume, further, the resistance of the tube to the motion of the gas to be, as is in reality the case, proportional to the length of the tube. If  $x$  be the distance between a certain section-plane and the open extremity of the tube, the resistance undergone in that plane by the motion can be put proportional to  $x$ . We neglect altogether the influence which may be exerted upon the resistance by the difference of density and velocity of the gas. Let  $D'$  denote the density of the gas at the above-mentioned plane, and  $D$  its density at the open extremity of the tube. Every one knows that, from the moment the motion in the tube has become constant, the excess  $D' - D$  is proportional to  $x$ . The density of the gas therefore goes on increasing from the open end of the tube to that at which the force acts. Suppose now the two extremities of the tube joined so as completely to enclose the moving mass of gas. The gas will evidently undergo in one portion of the tube an expansion equal to its increase of density in the other; and at the transition-point between the two portions it will have the same density as if it were at rest. If the tube is everywhere equal, this transition-plane (neutral plane) will divide the tube into two equal parts. At equal



distances from this plane the condensation on one side will be equal to the expansion on the other. If the resistance is greater in one part of the tube than in the other, the neutral plane will be displaced towards the part presenting the greater resistance; and the amount of the displacement will be that which is requisite in order that the resistance of the whole of this part (from the above-mentioned plane to the place where the force acts) may become equal to the resistance of the other part. If  $D$  is the density of the gas at the neutral plane,  $D'$  the density in a plane situated on the side where the gas is condensed,  $D' - D$  will be equal to  $am'$ , in which  $a$  is a constant, and  $m'$  is the resistance from the neutral plane to the plane in question. If  $D''$  represents the density of the gas in a plane situated on the other side of the neutral plane,  $D - D''$  will in like manner be equal to  $am''$ , if  $m''$  is the resistance between these two planes.

These well-known propositions have a direct application to the circulating æther. It possesses the properties of ordinary gases, in that the mobility of its molecules is considerable, so as to permit it to exert equal pressure in all directions. The fact that an electrified body is endowed with the same optical properties as in its normal state shows, as I have remarked in the above-mentioned memoir, that the elasticity of free æther is proportional to its density. Therefore what has been said in this investigation with regard to ordinary gases may also be applied to the æther. The only difference will be that the æther, whether compressed or expanded, will place itself at the surface of the galvanic conductor, since the æther molecules repel each other.

Let us suppose a galvanic circuit in which an electromotive force  $E$  excites the motion of the æther in one direction. The æther will therefore become denser on the side of the electromotive force towards which the current goes, and be rarified on the other side.

The neutral plane will have a position such that the galvanic resistance from this plane to the seat of the electromotive force will be equal in amount on both sides. Now let  $i$  denote the intensity of the current,  $D$  the density of the æther at the neutral plane, or, what amounts to the same, the density of the æther when it is at rest; let  $D'$ ,  $D''$  be its density at any two planes on the condensation side, and  $D'_0$ ,  $D''_0$  its density on the expansion side; and, lastly, let  $m'$ ,  $m''$ ,  $m'_0$ ,  $m''_0$  be the respective principal resistances from the neutral plane to the planes above mentioned. As the resistance is proportional to the intensity of the current, we shall evidently have

$$\begin{aligned} D' - D &= m'i, & D'' - D &= m''i, & -(D'_0 - D) &= m'_0i, \\ & & & & -(D''_0 - D) &= m''_0i. \end{aligned}$$

Now  $D' - D$ ,  $D'' - D$ ,  $D'_0 - D$ , and  $D''_0 - D$  are nothing else but the differences between the electroscopic tensions in the respective planes, the first two being positive, and the last two negative.

We obtain, then, the conclusion that *the difference between the electroscopic tensions of two planes is proportional to the intensity of the current, multiplied by the principal resistance between those planes.*

These deductions of Ohm's law, of the development of heat, and of the distribution of electroscopic tension at the surface of the conductor, are applicable only to the case in which there are solid and liquid bodies in the circuit, since only for those bodies is it proved that the total resistance is proportional to the intensity of the current.

### § 3.

The fact that electromotive force, or electric tension, need not exceed a certain limit in order that the current may be able to pass through a solid or liquid conductor, depends, then, according to the unitarian theory, on this—that the effective resistance opposed by a conductor of that sort is proportional to the intensity of the current. If the electromotive force is little, the intensity of the current will also be little, and consequently the resistance will become so feeble that the electromotive force will be able to overcome it. Experiment teaches us that it is quite otherwise with gases. To compel the current to pass through a column of gas a determined electric tension upon the electrodes between which that column is situated is necessary; if the tension is below the above-mentioned limit, the current will not pass. It is true that the insulating property exhibited by the gas must not be attributed to its effective resistance alone; in fact experiments have led to the admission of the rise, at the electrodes, of electromotive forces obstructing the propagation of the electricity by the gas. If the gas is nevertheless sufficiently dense, experiment has shown that the tension necessary for bringing about a discharge is proportional to the distance between the electrodes. The electromotive forces which have their seat upon the electrodes having no connexion with the distance which separates the latter, it follows that, when the gas has sufficient density, it is chiefly its resistance that constitutes the true cause of the discharge not taking place if the electric tension remains below a certain limit\*. We arrive, therefore,

\* The resistance of the gas diminishes when it is highly rarefied, while the electromotive forces which originate upon the electrodes are seen to increase; but it is not necessary to take that circumstance into consideration here.

at the result that the resistance opposed by a gas to the propagation of electricity cannot be proportional to the intensity of the current, as is the case with solid and liquid conductors. It is quite as impossible to admit, with Hittorf, that the resistance of gases is in inverse proportion to the intensity of the current; for in that case the resistance in a column of gas through which an infinitesimal current passes would be infinite. Now, at the discharge of a condenser, or the closing of a galvanic pile, the current is at first excessively slight. If Hittorf's hypothesis were true, the resistance of the gas would at first be excessively great, and the current could not begin to circulate. Consequently the resistance of a gas cannot in any case be inversely proportional to the intensity of the current. It is in the nature of things that the effective resistance of a column of gas should be proportional to the length of the latter. Therefore, if  $l$  denotes the length of the column, and  $r$  the resistance in the unit of length, the resistance will be proportional to  $rl$ ; and from what has just been said,  $r$  is neither directly nor inversely proportional to the intensity of the current or to the tension of the electrodes. Quite the contrary, experiments show that the tension necessary for the discharge is proportional to  $l$ , whence it follows that  $r$  is independent of the tension.

If we admit, in accordance with what has been said above, that the resistance of gases is independent of the intensity of the current, all the differences above stated, between gases, on the one hand, and both solid and liquid bodies, on the other, can be accounted for by the unitarian theory.

If the resistance or counterpressure opposed to the propagation of the current by a column of the gas of the length  $l$  and section  $1$  be called  $k$ , the total counterpressure in a similar column having the section  $a$  will be equal to  $ka$ , not to  $ki$  as is the case with both solid and liquid conductors. On multiplying this expression by the velocity  $h$  of the electricity, the product will be proportional to the mechanical work which is accomplished in the column during the unit of time. Now  $i = \delta ah$ , an expression in which, as has been said above,  $\delta$  is a constant. We obtain, then, for the work done in a column of length  $1$  and section  $a$  the expression  $\frac{ki}{\delta}$ , to which the quantity

of heat developed in the same column must be proportional. The quantity of heat developed in a column of gas will therefore be proportional to the intensity of the current, but independent of the section of the column.

The resistance being determined by the counterpressure which the conductor opposes, on the unit of section, to the

propagation of the electricity, and this counterpressure being, in gases, independent of the intensity of the current, it is self-evident that the resistance of a column of gas must be independent of its section.

The difference of electroscopic tension between two points in the conductor situated at a certain distance from each other is, according to the foregoing, proportional to the resistance between the same points. In solid and liquid conductors, therefore, the difference of tension will be proportional to  $ri$ , if  $r$  denotes the principal resistance between the points, and  $i$  the intensity of the current. For gases, on the contrary, the same difference will be proportional to  $kl$ , in which  $k$  has the signification which has just been mentioned, and  $l$  denotes the distance between those points. The difference of electroscopic tension between two points in a column of gas must, then, as has already been proved by experiment, be independent of the intensity of the current; and it can be predicted that it will also be independent of the section of the column, which, however, has not yet been confirmed by experiment.

If  $r$  designates the principal resistance in the part of a closed circuit composed of solid and liquid conductors,  $R$  the resistance of a column of gas introduced into the circuit,  $E$  the electromotive force,  $i$  the intensity of the current, and  $L$  the total length of the conductor, the differential equation of motion of the æther will be

$$L \frac{di}{dt} = nE - nR - nri.$$

From this equation we get, for the case in which the current has had time to become constant,

$$i = \frac{E - R}{r}.$$

The resistance  $R$  of the gas has therefore in reality its place in the numerator, although, according to the ordinary formula of Ohm, it ought to be in the denominator. Of course  $E$  must be greater than  $R$  for a current to be possible.

If, when gas is introduced into the circuit,  $i$  and  $i_1$  denote two different current-intensities answering to the resistances  $r$  and  $r_1$  of the solid and liquid conductors introduced into the circuit, and if  $M$  and  $M_1$  are the resistances necessary in order to produce the same current-intensities when the gas is excluded from the circuit, we get

$$i = \frac{E - R}{r} = \frac{E}{M}$$

and

$$i_1 = \frac{E - R}{r_1} = \frac{E}{M_1},$$

whence

$$\frac{i_1}{i} = \frac{r}{r_1} = \frac{M}{M_1} = \frac{M - r}{M_1 - r_1}.$$

If, as was done in the calculation of Becquerel's experiments,  $M - r$  and  $M_1 - r_1$  were made to signify the resistance of the gas at two different current-intensities, the resistance of the gas would be found inversely proportional to the intensity of the current, although in reality it is independent of that intensity.

#### XXIV. *On the Violet Phosphorescence in Calcium Sulphide.*

*By Captain W. de W. ABNEY, F.R.S.\**

IN some investigations in photography it became necessary that I should study the phenomenon of phosphorescence exhibited in calcium sulphide, such as is employed in Balmain's paint. And as one or two points of interest arose which have not (as far as I am aware) been described before, I have thought it might be of interest to lay the subject before the Society.

The phosphorescent light, which is a peculiar violet, can be generated, if I may use the term, by day-light or candle-light—by the former fairly brightly, and by the latter only feebly, for reasons which will appear. In order to gain strong phosphorescence, the light from a magnesium-ribbon or the electric light should be employed. Mr. Warnerke has shown that  $\frac{1}{8}$  inch of ribbon of the former is sufficient to excite phosphorescence to the maximum point that can be obtained from light of that brilliancy. Light of greater brightness, however, seems to excite it even more strongly. In a communication made to the Society by Lieut. Darwin, R.E., he gave the formula for the decrease of phosphorescence after excitation, from which it will be seen that it very rapidly diminishes in brilliancy.

My first experiment was to determine the spectrum of the emitted light; and this I observed with a small spectroscope; and the emission-spectrum is shown in I, figure opposite. It will be seen that to the eye the greatest luminosity is between G and F, and a feebler one extending from between E and F

\* Communicated by the Physical Society, having been read at the Meeting on January 28, 1882.



as far as the eye can recognize colour of low intensity towards the red. It became a matter of curiosity to know if any rays lay beyond the violet; and for this purpose an Iceland-spar prism and quartz lenses to the collimator and camera were brought into requisition, together with extremely sensitive photographic plates. Glass was spread with a layer of this sulphide and held together by paraffin as a substratum; the phosphorescence was excited by the electric light, and the tablet held in front of the slit. The exposure lasted one minute, when the phosphorescent tablet was again excited, and used as a source of light as before. After forty such excitations the photographic plate was developed; and a band (shown in II.) was registered, which absolutely coincided with the band already registered in the visible spectrum. There was no trace of any radiation having wave-lengths in the ultra-violet. Whether there is any radiation below the red is a moot point; but from the gradually increasing brightness of the spectrum in the yellow, it seems probable that there is such.

The next point to ascertain was the part of the spectrum which excited phosphorescence. A tablet similarly prepared was exposed to the spectrum of the electric light, which showed carbon-bands strongly just above H, and also in the violet near G. A sensitive photographic plate was placed in contact with the tablet, and allowed to remain in contact 40 seconds, after which it was developed. III shows the



locality of the spectrum by which phosphorescence was excited. This agreed absolutely with the visual observations. The exact locality was fixed by the carbon-bands above alluded to, and also by comparing it with a sensitive photographic plate exposed in the ordinary manner. It will be noticed that the ultra-violet rays do not seem to cause phosphorescence in this case.

It now remained to register those rays which destroy the phosphorescence. This was effected in the following manner:—A tablet was first excited, and after half a minute exposed to

the spectrum: those rays which destroyed phosphorescence were distinctly visible, as were also those which excited it. The tablet was placed in contact with a sensitive plate and developed. The wave-lengths were determined by placing a liquid in front of the slit and noting the place where the known absorption-bands in the infra-red region occurred, which is here shown by these localities remaining of the same luminosity on the tablet surrounding the impressed spectrum. The rays which destroy phosphorescence of this description are shown in IV. It will be noted that in the infra-red region is a portion which does not destroy it. When the wave-lengths of this are compared with the wave-lengths of the exciting portion about G and H, it is found that they are octaves one to another. (In the figure the infra-red region is much compressed, owing to the spectrum used being a prismatic spectrum.)

This fact appears remarkable and worthy of note. My own impression is that another band below this may also be traced; but as it was not shown upon the photographic plate, I have not mapped it. Such a band would probably be another octave below the second band. It should be noted that the infra-red band apparently is of the same luminosity as the general luminosity of the plate, and that these rays only feebly excite the plate.

I have endeavoured to make out any spectral difference in the light excited about H and about G, and have failed to obtain evidence as to any alteration in colour. It seems indifferent whether phosphorescence be excited by the indigo or by the violet rays.

I am at present engaged upon other phosphorescent material.

## XXV. *Notices respecting New Books.*

*Leçons sur l'Électricité et le Magnétisme.* Par E. MASCART et J. JOUBERT. Tome I. Paris: G. Masson. 1882.

THIS is a work whose value is not to be judged on its absolute merits, though these are in many places of a high order. Like the former treatise by M. Mascart, it is to be looked on as intended to fill an almost absolute gap in modern French scientific literature. The nation that once could boast of Fourier, Lagrange, Laplace, and Poisson, has never since been without worthy representatives in the front ranks of mathematicians. Galois, Cauchy, Leverrier, and Chasles are names never to be forgotten; and the veteran Liouville, with De Saint-Venant, Hermite, and others, still uphold in that department the prestige of the Academy of Sciences. But the successors of Ampère and Sadi Carnot—masters of the still higher art of applying mathematical reasoning to new fields of

physics—must now be sought in Britain and in Germany rather than in France; the newer great branches of Applied Mathematics have been, till recently, almost ignored there. The Theory of Heat has remained, so far as France is concerned, almost confined to the region so thoroughly and so charmingly explored by Fourier; the real value of Carnot's wonderful treatise was first pointed out by Thomson. That treatise has supplied the Second Law of Thermodynamics, and some of the grandest scientific generalizations ever made. But this was not done in France. Ohm's little adaptation (to electricity) of one of the merest elements of Fourier's great work has been developed in Britain and in Germany into one of the most extensive and most rapidly growing branches of physics—profoundly valuable alike in theory and in practice—which, till quite recently, was practically known only in its beggarly elements to the most illustrious of French scientific men. Some detached portions of Faraday's splendid discoveries were no doubt developed in France, but only as isolated facts; the grand chain of deductive reasoning by which he was led to them, and by which he coordinated them, was almost completely ignored. Where shall we seek for a modern French work containing any thing new on Vortex-motion, on Discontinuous Fluid-motion, on the Kinetic Theory of Gases, or on the theories of Anomalous Dispersion or of Fluorescence? Where for a contribution to the more modern treatment of the size of the grained structure of matter? The best of recent French scientific men seem to have been content to work only on *some* of the lines of *some* of their more illustrious predecessors. Fizeau, Foucault, and Cornu are worthy successors of Fresnel; but Ampère has had no successor in France. All countries appear to pass through these peculiar phases of arrested development. Newton's grand achievements effectually paralyzed, for a century at least, the progress alike of pure mathematics and of the true theory of light, so far as his own countrymen were concerned. Young's brilliant career made ample amends for this in the matter of the Theory of Light; but we had to take our mathematics from France and Germany in the first quarter of the present century. It would seem that it is next to be Germany's turn for a partial eclipse of a similar kind. Gauss and Riemann have made possible the existence there of names as great as their own—Helmholtz and Kirchhoff, for instance; but the men of the rising generation seem to be satisfied, like the French for the last fifty years, or like the British for a century after Newton, merely to swear by (and comment upon), while infinitesimally extending, the words of their *own* present Masters. It is this self-containedness, so to speak, that arrests the growth of science in a nation. The human family, in its every branch, needs all the help it can get from the other branches; and the real reason for France's present deficiency in the theories of Heat and Electricity is its fatal neglect of *every thing not written in French*.

The recovery in France, first seriously set afoot by the lamented

Verdet, seems now really likely to progress ; and all men of science will hail with satisfaction the well-conducted efforts which M. Mascart has made to promote it. What an enviable position he occupies ! To be the first, or practically the first, to instruct his countrymen in the great life-work of Clerk-Maxwell ! to open to them the storehouses filled to overflowing with marvels by Helmholtz and Thomson ! to show them, once for all, that great as may be the services of an individual, or even of a race, science progresses with almost infinitely greater rapidity by the mutual action between individuals and between races—the more widely different they are the better !

After what we have said, it would be improper to formally criticise the work before us. Almost all of its contents have been long known to those whom they concern, alike here, in Germany, and even in Italy. When Babbage, Herschel, and Peacock introduced the more modern mathematics into England, they contented themselves with modestly translating Lacroix's work ; and we might be tempted to think that a translation of Clerk-Maxwell's 'Treatise on Electricity' would have been a greater boon to France than the present work. But a large amount of the *matter* of that work is here ; and that, after all, is the chief question. It is too much overlaid, however, with details of small contributions to the science, whose place might advantageously have been supplied by theorems of a higher value. There is therefore, here and there, rather a superfluity of sack ! But the authors seem to have mastered fully the leading features of the most modern treatment of the subject ; and they have put these in forms (always clear and neat as it is the peculiar privilege of their countrymen to be able to do, while) sometimes considerably improved from those in ordinary use either here or in Germany. One great defect, however, we cannot pass over. This is the absolute want of references to the various original sources of information, though of course the authors are named. This is totally indefensible. Without occasional, and often frequent, study of original memoirs, little good progress can be made ; and a few additional pages would have added infinitesimally to the cost of so large a work, while enormously increasing its value.

We do not suppose that the work is likely to have much circulation out of France ; but that is of little moment. Let us hope that M. Mascart's countrymen will avail themselves of this excellent opportunity of attaining the higher level of this fascinating subject, which is at present temporarily occupied by some of their neighbours. Once raised to that level, they are very unlikely (if the past furnishes any criterion) soon to fall again below it. There seems to be little doubt that it is from the point of view furnished by electrical phenomena, properly coordinated and comprehended, that the next really great advances in physical science are to be looked for. He who discovers the true *mechanism* of friction, of thermo-electric currents, and of electric inertia, will take a step of quite as important a character as that which Newton took with regard to Gravitation or Huyghens with regard to Light.



*An Old Chapter of the Geological Record with a New Interpretation, or Rock Metamorphism (especially the Methylosed kind), and its resultant Imitations of Organisms: with an Introduction, giving an Annotated History of the Controversy on the so-called Eozoon canadense, and an Appendix.* By Professors W. KING, *Sc.D. &c.*, and T. H. ROWNEY, *Ph.D. &c.* London: Van Voorst.

THE present volume is the latest outcome of the *Eozoon* controversy. It commences with an introduction of fifty-seven pages, more than one fourth of the whole book, giving an epitome of the literature (already formidable) which the discovery, rather less than a quarter of a century since, of this supposed fossil has already evoked. The different publications are arranged in chronological order, with abstracts of their principal contents. This is a valuable part of the authors' work, and will form a useful compendium of the literature of the subject. It would, however, have been still more valuable had it not been annotated, or if Messrs. King and Rowney had been able to refrain from passing sarcasms, which are often, to say the least, in bad taste, and occasionally, from their obvious unfairness, arouse in the reader's mind a feeling of scepticism as to whether the authors could possibly do justice to the views of an adversary. They may no doubt plead in extenuation that they are not the only sinners in this respect, perhaps that they were not the first to import bad temper into a scientific discussion; at the same time, they would certainly have improved their position, if they had preserved their equanimity in the historical part of their work, and reserved their sneers and retorts for the more controversial portion.

The work itself discusses, after two or three preliminary chapters on "ophites" in general, some wider questions concerning mineralized and methylosed metamorphic rocks. By the former of these terms is meant a rock which has had "the original substance of its members crystallized into minerals of various kinds;" by the latter, one which has had "the same minerals altered or replaced by chemical reactions." The distinction—which, however, is perfectly well known to all petrologists, though the authors seem to treat it as if it were a discovery—is undoubtedly an important one, though in practice it is often by no means easily maintained; and we may consequently doubt whether it was worth while cumbering the literature of science with another word of foreign origin. The work next passes on to discuss the origin of ophites. Here the authors point out that serpentinization is effected in certain deposits without the intervention of mineralization; that many ophites were originally sediments, others igneous rocks; and discuss the origin of hemithrene and other related calcitic rocks. Then comes a chapter on the minerals characteristic of ophites and related rocks, especially of peridote, followed by some on the origin of crystalline limestones, dolomites, &c., and on the age of ophites.

A lengthy appendix follows, treating of various questions, some of them rather remotely connected with the subject-matter of the



book. One of these also exhibits the authors' fondness for "comfortable words" from tongues not generally understood by the vulgar, as it is entitled *Thalassa* and *Xera* in the Permian Period. We are doubtless glad to learn that Messrs. King and Rowney understand Greek, or at any rate know enough of it to use an English-Greek lexicon; but we fail to see why, in this matter, plain English would not have equally well expressed their meaning.

The work is illustrated by nine plates and some woodcuts. The latter are only diagrammatic; the former are far from well executed. Whether this is the fault of the authors or of their lithographers we are, of course, unable to decide; we may, however, say that in other cases where we have found our leaning (to which we confess) towards the organic origin of *Eozoon* somewhat shaken by their assertions and arguments, we have felt our faith is refreshed by turning to their illustrations, which represent structures, like those upon which Dr. Hahn\* has lately expended so much pains, which to our eyes have only a rough general resemblance to those unquestionably organic, or claimed as such, in the best specimens of *Eozoon*.

The book, we may add, is not well edited. A long list of *corrigenda* is given; and there are several other mistakes which have altogether escaped the authors' notice. Some are no doubt merely printer's errors; but others are sufficiently grave to show a want of due care in passing the work through the press.

We do not purpose in our present notice to enter into the vexed question of the nature of *Eozoon canadense*, further than to say that the present work contains a very full statement of the authors' reasons for believing it to be only a mineral structure; and a large amount of curious and instructive matter is brought together which deserves to be well considered by those who incline to the other view.

We pass on, then, to some questions of a more general nature raised by the present work. First, as to the classification of ophites in the opening chapter, which is "offered indeed," as they state, "more for practical purposes than as being a natural one, though it is not altogether devoid of the last character." It is as follows:—

#### A. SILACID OPHITES.

Serpentinytes.

Talc schist, Rensselaeryte (potstone).

Sepiolytes, Magnesio-argillyte ("Argille magnésienne," *Delesse*).

\* In reference to this we may, in passing, note a paragraph in the American journal 'Science,' which states (vol. ii. p. 410) that Dr. Hahn exhibited his slides to Mr. C. Darwin, who had no sooner "peered through the microscope on one of the finest specimens, when he started up from his seat and exclaimed 'Almighty God! what a wonderful discovery! wonderful!' and after a pause of silent reflection he added, 'Now reaches life down!'" A story so circumstantial one would think must needs be true; but we have the best authority for characterizing it as simply fabulous.

a. *Sub-silacid Ophites.*

Chlorargillytes.

Agalmatolytes.

Chlorite-schists, Hydro-phlogopite schists.

Talc gneisses (Protogines).

Peridolytes\* (Lherzolyte, Dunyte, Picryte, Ossipyte, &c.)

Ophi-euphotides.

B. SILO-CARBACID OPHITES.

Ophi-calcites.

Ophi-magnesites.

Ophi-dolomites.

b. *Sub-silo-carbacid Ophites.*

Malacolophytes.

Hemithrenes.

Calci-micaschists.

&c. &c.

Putting aside all questions as to the nature of *Eozoon*, we confess ourselves entirely at a loss to understand the principle of this classification. Clearly it is neither petrological nor mineralogical. In a work purely chemical, an arrangement which depends solely on chemical composition might be allowable. In certain cases also it might be of advantage to pay regard solely to mineral constituents; but inasmuch as the scope of the authors' work is, to say the least, distinctly petrological, we must protest against one which groups together rocks which not only differ markedly in structure, but also, by the authors' own admission, are sometimes of igneous, sometimes of sedimentary origin. Further, we are at a loss to determine what principle underlies the above classification. At first we supposed it to be chemical, and that Ophite, in the authors' minds, was equivalent to "a rock characterized by the presence of minerals containing silicate of magnesia," *i. e.* in which this is an important constituent; but we are baffled by finding among the members (and that, too, next the "Peridolytes,"—*i. e.* rocks consisting mainly of silicate of magnesia), talc-gneisses (Protogines). In the latter, if the authors use the word Protogine in the ordinary sense (*i. e.* to designate such a rock as we find in the heart of the Mont Blanc *massif*), even the presence of talc is disputed by some authorities, and in any case it is certainly subsidiary; for the percentage of magnesia, in all the analyses which we have seen, is extremely small. Such a classification, then, rests on no principle whatever, and is only calculated to throw the student into hopeless confusion, traces, indeed, of which are to be detected in the book itself. The authors do not appear to have clearly made up their

\* We are at a loss to understand why the authors persistently write this word as above. The recognized textbooks always have it Peridotite, or (to follow another spelling of the authors in which they are not always consistent) Peridotyte; and as it is named from the mineral Peridote, this seems the only possible orthography. Is this an example of *methylosis*?

minds as to what is meant by the word serpentine. For this there is, no doubt, excuse in the fact that few names have been used more vaguely: the unfortunate accident that the same name has been applied to a mineral and a rock (an accident which the authors themselves attempt to remedy in the case of dolomite, and should in very consistency have done in this also) has tended much to cause this confusion. It has been augmented by the general neglect of petrology by English geologists; we had almost written the contempt, all but expressed for it, by not a few of the more eminent among them. It has been further augmented by the fact that rocks which chemically, mineralogically, and sometimes petrologically, widely differ from true serpentines, to the unaided eye resemble the latter; so that a rock which is only serpentinous may often, at first sight, be mistaken for a serpentine,—this being a rock consisting chemically of about 39 per cent. of silica, 36 per cent. of magnesia, with probably about 12 per cent. of water, and 7 per cent. of iron oxides, and rather variable quantities (usually not exceeding, and, except in the case of the first, almost always less than 2 per cent.) of alumina, lime, nickel, &c.—a rock, in short, which, chemically, lithologically, and petrologically may be represented by the serpentine of the Lizard. There being then such a type in not a few regions, a nomenclature which neglects it, and a classification like the above, appear to us as objectionable and as fatal to all progress in petrology as it would be to put a basalt with a clay slate, because examples might be found containing about the same proportion of alumina: indeed we are much perplexed at not finding the former rock inserted in the above classification, seeing that it certainly contains a considerable percentage of magnesia.

An instance of the confusion which the above hazy definition of ophites has caused in the minds of the authors themselves (or possibly a proof of their inability to view a question judicially) may be found in their introduction (p. xlv), where they state they are unable to understand how a writer can “believe in the organic nature of *Eozoon*” and yet assert “that he has never seen a serpentine which was not intrusive.” To this they append the remark, it “is a puzzle to us, as it must be to Eozoonists, considering that their doctrine is based on the sedimentary or aqueous deposition of eozoneal serpentines. But is not eozoonism full of inconsistencies?” Any careful reader will see at a glance that the guarded statement in the last clause is not equivalent to saying “there is no serpentine which is not intrusive.” The context also of the letter quoted, and every paper which we can remember published by the author cited, always uses the term serpentine in the strict sense mentioned above. Further, there is no more inconsistency in believing that serpentine (mineral) may occur sometimes in a rock of igneous, sometimes of “aqueous” origin (assuming that the mineral in the eozoneal “ophicalcites” is serpentine) than in stating that quartz-crystals are found both in trachytes and in the interior of organisms in Cretaceous deposits. Indeed, if we remember aright, the above author has been at some pains to show that, even in the true ser-

pentine rock, the mineral is a secondary product. This confusion is continued in the authors' speculations as to the origin of such serpentines as that of the Lizard. It has been shown during the last few years by several independent observers that, chemically and microscopically, there are the strongest reasons for believing that these serpentines are in all cases altered peridotites. The process of transition from the wholly unaltered olivine rock to that in which every characteristic structure of the olivine has been obliterated has been laboriously traced and described; yet Messrs. King and Rowney simply reiterate their opinion, that it has been derived by methylosis from a "dolerite (wacke or melaphyre) like that of Bufaure in the Tyrol" \*. No suggestions are made as to the means by which the large percentage of silicate of alumina (necessarily present in the felspar of a dolerite, and usually a very obstinate constituent, declining to yield to this kind of methylosis action) has been removed; and but little confirmatory evidence is adduced beyond the vague statements of authors who lived before the microscope was applied to petrology. In the same hasty way, the bronzite crystals in the Lizard serpentine are held to be pseudomorphs after black augite; and a chemical and microscopical demonstration that they cannot be distinguished (allowing for partial hydration) from varieties of enstatite is cited as confirmatory of their idea that the "crystals are pseudomorphs of chlorite after augite."

We do not deny the possibility of the alteration of augite into a mineral which might be mistaken for enstatite or bastite; but after a considerable experience in the microscopic study of augite and its changes, we could not accept the statement without a clear demonstration.

The above case, however, is simply illustrative of a tendency which runs through and vitiates the whole work, viz. to postulate the very points which are of vital importance to the argument, and which are denied by not a few authorities at least as experienced as the authors themselves. The following are a few instances of begging the question:—Augite and hypersthene are placed among mineral species "common to ordinary metamorphics." The authors are surely aware that at any rate normal augite cannot be called common in metamorphic rocks, and that the metamorphic origin of any important mass of hypersthene rock is a matter of dispute. The "green marble of Connemara" is assumed to be post-Archæan, and the Upper Gneiss series of Scotland Lower Silurian; but the

\* The authors' remark about the opinion that "ophite, or its essential component serpentine," has originated from peridotite rock, is in itself a proof of their hasty way of looking at an adverse opinion. "It cannot be denied that the common occurrence at Snarum of pseudomorphs of serpentine after peridote, and the frequent association of the two minerals in other places, may be taken as good evidence in favour of this view; but it would be just as reasonable to assume that basalt, because it usually contains a large proportion of peridote, was generated out of masses of this mineral." *Just as reasonable!* Is there any evidence of the replacement of olivine by a lime-felspar, accompanied, too, as it would here be, by an entire change of the intimate structure of the rock?



age of all the metamorphic rocks of Scotland and Ireland must be regarded, after the conflicting statements of the last few years, as still an open question; and, though the authors are more cautious here, we may extend the remark to their comments as to the Alpine gneisses and schists. While on that topic, we may note that they appear to be ignorant that the metamorphism of the great dolomitic masses of the Tyrol differs greatly from that of the Alpine gneisses and schists. Indeed, unless it be proved that the magnesian constituent is the result of methylosis, these masses are no more metamorphic than most of the British Carboniferous limestone. In fact they are just as much and just as little metamorphosed as the Permian dolomites (on which, by the way, the authors make some valuable remarks which are a real contribution to the perplexing history of this rock). A similar want of caution characterizes the following remark:—"Studer long ago discovered ammonites and belemnites in a similar but less crystalline deposit (that is, a crystallized limestone associated with gneiss on the Jungfrau), lying between gneisses at Mettenberg, near Grindelwald" (p. 32). Those who know the region will hesitate to accept the apparent induction without clearer evidence than is generally produced in this and, we may add, other cases. Some also of the citations of opinions, apparently favourable, are only true when the word "ophite" is used in the vague sense in which the authors employ it.

We had purposed to comment upon two other subjects mentioned by the authors—the "striping of triclincic felspars," and the secondary origin of peridotite; but space will not allow us to say more than that the former structure, although evidently a puzzle to them, is generally held to be the result of twinning, and that their arguments on the latter question appear to us as ingenious and as unconvincing as those by which Daubuisson proves that basalt is of "aqueous origin."

*Journal and Proceedings of the Royal Society of New South Wales.* 1880. Vol. XIV. Edited by Prof. A. LIVERSEDGE. 8vo, 392 pages. With ten Plates. Sydney, 1881.

IN this volume, astronomy, meteorology, botany, organic and inorganic chemistry, lithology, mineralogy, palæontology, and the study of local water-supply are all and each made sources of information to the world at large, as well as to the Society in particular, by some twelve of its energetic members. There is also an elaborate report on morbid psychology, treating of the causation and prevention of insanity, by one of its medical members.

## XXVI. *Intelligence and Miscellaneous Articles.*

ON THE FORMATION OF PEROXIDE OF HYDROGEN DURING COMBUSTION. BY ALOIS SCHULLER.

WHEN determining the heat of combustion of hydrogen\*, I remarked during the combustion of oxygen in hydrogen, besides the usual very small flame, a second, much larger, blue so-called

\* Schuller, Wied. *Ann.* ii. p. 373 (1877).



flame, the closer investigation of which led to the conclusion that during the combustion of oxygen and hydrogen, under certain circumstances, peroxide of hydrogen is also produced. As this subject has not, to my knowledge, yet been thoroughly discussed, I will briefly communicate the experimental results which up to the present time I have obtained.

As previous experiments had already indicated that the blue flame is conditioned by accidental circumstances, I sought before all things to ascertain these. It then appeared that the flame is not visible when hydrogen burns in oxygen, but only on the combustion of oxygen in hydrogen, provided that both are free from atmospheric air,—and, further, that it comes out better when to one of the gases a little sulphurous acid is added, while it disappears if the gases are passed over potassium hydrate. In consequence of this I removed the sulphuric acid (from which the gases appear to have taken up a trace of sulphurous acid) from the gas-holder. The blue flame was now no longer visible; but it immediately became so after the addition of sulphurous acid. The different experiments all led to concordant results, whether a smaller or a larger combustion-space (from 5 to 500 cub. centim.), or gases produced by electrolysis or otherwise were employed. All this shows that the blue flame stands in connexion with the sulphurous acid contained in the gases.

During these experiments the water formed each time was also examined. A trace of sulphuric acid was found in it as often as the blue flame was visible, which was absent whenever the latter did not appear. Besides this, the water usually took up some peroxide of hydrogen, which was proved by iodide-of-zinc starch and sulphate of iron, by permanganate of potassium, and by the so-called perchromic-acid reaction.

These in themselves interesting facts formed the subject of further experiments. First of all I convinced myself that, under certain conditions,  $\text{H}_2\text{O}_2$  is produced both when  $\text{H}$  burns in  $\text{O}$  and when  $\text{O}$  burns in  $\text{H}$ , but that the amount differs very much, according to the conditions of the experiments. Of essential importance is the velocity with which the burning gas penetrates that which surrounds the flame: if this velocity is very inconsiderable, traces only of  $\text{H}_2\text{O}_2$  appear, while with considerable excess of pressure striking reactions are obtained. Thus, in one case, during the combustion of oxygen in hydrogen at the temperature of the room, I obtained water containing 0.0008 gram  $\text{H}_2\text{O}_2$  in 1 gram, therefore nearly 0.001 of the whole; and it appears to me very probable that under more favourable conditions considerably more might be produced. The presence of  $\text{SO}_2$ , while, on the one hand, it conditions the blue flame, diminishes the amount or prevents the occurrence of peroxide of hydrogen; at the same time the corresponding amount of sulphurous is converted into sulphuric acid. These, as well as other experimental results, indicate that the blue light has its origin in the combination of  $\text{H}_2\text{O}_2$  and  $\text{SO}_2$  to form  $\text{H}_2\text{SO}_4$ .

These circumstances explain, on the one hand, why in the above-mentioned calorimetric measurements no peroxide of hydrogen could be demonstrated (for in the slow combustion no more appears to have been formed than was necessitated by the minute quantity of sulphurous acid contained in the gases), and, on the other, why the amount of sulphuric acid contained in the water was so small; it appears to have arrived in the combustion-space not as sulphuric, but as sulphurous acid.

The same circumstances seem also to explain the green edge shown by the hydrogen-flame when iodine is present. The simultaneous formation of iodic acid, which has been pointed out by G. Salet\*, may probably be connected with the occurrence of peroxide of hydrogen.

After these facts it appeared probable that in the third case of the combustion also, viz. during the explosion of oxyhydrogen, besides water, peroxide of hydrogen is produced, which supposition was confirmed by experiment. It could be demonstrated in all the experiments made in relation thereto: a scarcely perceptible quantity of the water formed in the explosion gave the iodine reaction; and a drop was sufficient to show strikingly the perchromic-acid reaction.

During explosion the peroxide of hydrogen appears to be formed in still larger quantity than in ordinary combustion; but I have not yet succeeded in carrying out a reliable quantitative determination, because all the tubes employed, of the length of about 1 metre, were shattered. These unsuccessful experiments, however, led to an in other respects interesting result:—All the tubes were very strong, so that one of the weakest required a *continued* pressure of 100 atmospheres to burst it. To this must be added that it was always only the part most distant from the place of ignition that was burst, even when, with 3 millim. thickness of wall, its bore was only 3–4 millim. in diameter—whence it follows that very pure oxyhydrogen, such as I employed, occasions in long tubes, in the part furthest from the place of ignition, a pressure of hitherto unsuspected magnitude. This holds good even when the tubes are narrowed by one or two coils of cord to 2 millim. internal diameter; but a slight content of air modifies the result considerably. I believe that this can be accounted for as follows:—In consequence of the considerable pressure arising at the place of ignition, the still unburnt gas is driven with great velocity along the tube; hence the slowly spreading ignition meets continually with more and more powerfully compressed gas; wherefore the pressure in the corresponding part of the tube increases more and more, till finally, at the end of the tube, the most violent action takes place. In my experiments the pressure there was much greater than it can have been, according to Bunsen†, in the most favourable case of simultaneous ignition of the entire mixture.

\* *Comptes Rendus de l'Académie des Sciences*, lxxx. p. 884 (1875).

† Bunsen, *Gasometrische Methoden*, (1875) p. 256; cf. (1877) p. 331.

The driving forward of the oxyhydrogen gas here supposed has also been assumed by Mallard and Le Chatelier\*, in order to explain the increase of the velocity of propagation of the ignition observed by them.

From what has been adduced, it follows, *inter alia*, that in precise determinations of the heat of formation of water the  $H_2O_2$  formed must also be taken into account, and, further, that, in the case of explosion, the loss of heat occasioned by the breaking must be taken into consideration.—Wiedemann's *Annalen*, 1882, no. 2, vol. xv. pp. 289–292.

ON THE LAW OF RADIATION. BY J. VIOLE.

The intensity of a simple radiation emitted by incandescent platinum is very accurately represented by the formula

$$I = mT^3(1 + \epsilon\alpha^{-T})^T,$$

as I have previously pointed out, and as is proved by the following Table, which contains the values calculated by means of this formula for a portion of the measurements before mentioned :—

<i>t.</i>	$\lambda = 656 \left\{ \begin{array}{l} \epsilon = 0.041495 \\ \alpha = 1.00045. \end{array} \right.$		$\lambda = 589.2 \left\{ \begin{array}{l} \epsilon = 0.04295 \\ \alpha = 1.00044. \end{array} \right.$		$\lambda = 535 \left\{ \begin{array}{l} \epsilon = 0.04467 \\ \alpha = 1.00043. \end{array} \right.$	
	Calculated intensities.	Differences from the observed.	Calculated intensities.	Differences from the observed.	Calculated intensities.	Differences from the observed.
775°	...	...	0.05	0	...	...
954	1	0	1	0	1	0
1045	3.1	-0.2	3.4	-0.2	3.6	-0.1
1500	153	0	218	-1	324	+17
1775	501	-6	812	+3	1365	0

But if the attempt be made to represent by the same formula the numbers of Dulong and Petit relative to the radiation of their thermometer between 80° and 240°, good results are not obtained. Nor does the celebrated formula of those two physicists,  $I = m\alpha^t$ , agree with the measurements obtained with incandescent platinum; and the expression  $I = mT^4$ , recently proposed by M. Stéphan, giving for the relative intensities at 954°, 1045°, 1500°, and 1775° the numbers 1, 1.33, 4.36, and 7.73, cannot be adopted.

On the other hand, a very satisfactory representation of the whole of the measurements is obtained by means of the formula

$$I = mTbT^2\alpha^T,$$

in which  $T$  represents the absolute temperature,  $m$  a constant coefficient,  $b$  the number 0.9999938,  $\alpha = 1.03550 - 13\lambda$ ,  $\lambda$  being the wave-length in millimetres.

In fact, if we apply this formula, first, to the platinum radiation, we shall have :—

\* *Comptes Rendus*, xciii. pp. 146, 147 (1881).

<i>t.</i>	$\lambda=656.$		$\lambda=589.2.$	
	Calculated intensities.	Differences from the observed.	Calculated intensities.	Differences from the observed.
775 <sup>0</sup> .....	...	...	0.04	-0.01
954.....	1	0	1	0
1045.....	3.0	-0.3	3.2	-0.4
1500.....	161	+7	219	0
1775.....	507	0	807	-2

<i>t.</i>	$\lambda=535.$		$\lambda=482.$	
	Calculated intensities.	Differences from the observed.	Calculated intensities.	Differences from the observed.
954 <sup>0</sup> .....	1	0		
1045.....	3.4	-0.3		
1500.....	311	+4	142	1
1775.....	1371	+6	807	5.7

The calculations were made with the values of  $\alpha$  which appeared to accord best with the observations. These values,

$$1.02713, \quad 1.02772, \quad 1.02838, \quad 1.02935,$$

satisfy the formula  $\alpha=1.03550-13\lambda$ , with the respective differences

$$-0.00016, \quad +0.00012, \quad +0.00015, \quad -0.00012.$$

The experiments of Dulong and Petit are equally well represented by the same formula, assuming  $\alpha=1.01161$ ,—that is to say, supposing  $\lambda=1838$ , which is perfectly admissible according to the measurements of M. Mouton, who has determined the wavelengths up to 2140. We have, in fact:—

Excess.	Velocity of cooling.		$\Delta.$
	Determined by Dulong and Petit.	Calculated by my formula.	
80 .....	1.74	1.71	-0.03
100 .....	2.30	2.35	+0.05
120 .....	3.02	3.10	+0.08
140 .....	3.88	3.97	+0.09
160 .....	4.89	4.96	+0.07
180 .....	6.10	6.10	0
200 .....	7.40	7.39	-0.01
220 .....	8.81	8.84	+0.03
240 .....	10.69	10.46	-0.23

The differences are not, in general, greater than those existing between the numbers calculated by Dulong and Petit from their formula and the observed numbers.

From the whole of these facts it appears to me to follow that, between  $0^\circ$  and  $1775^\circ$ , the law of radiation can be represented by the formula

$$I = mTbT^2\alpha T.$$

*Comptes Rendus de l'Académie des Sciences*, t. xcii. p. 1204.

#### ON WHEATSTONE'S BRIDGE. BY K. F. SLOTTE.

The length of the platinum wire belonging to this apparatus, which cannot be exactly determined by measurement, can, it is well known, be ascertained indirectly by comparing and exchanging resistances\*. The following procedure is a modification of this method which may not be without advantages.

Let  $s$  be the length of the wire,  $a$  and  $b$  that of its two divisions when two resistances  $w_1$  and  $w_2$  are inserted and the galvanometer shows no current. Then is

$$\frac{w_1}{w_2} = \frac{a}{b} = \frac{s+a-b}{s-(a-b)} = \frac{s+d_1}{s-d_1}, \dots\dots\dots (1)$$

in which  $a-b$  is put  $= d_1$ . If now the resistances  $w_1$  and  $w_2$  be exchanged and the movable contact shifted till again no current passes through the galvanometer, this displacement, taken as positive or negative according to whether  $a$  is more or less than  $b$ , is equal to  $d_1$ , which quantity can be directly determined by reading it off upon the scale of the apparatus.

If in the same manner  $w_2$  be compared with a third resistance  $w_3$ , and, again,  $w_3$  with  $w_1$ , and if the displacements corresponding to  $d_1$  be denoted respectively  $d_2$  and  $d_3$ , then we have

$$\frac{w_2}{w_3} = \frac{s+d_2}{s-d_2}, \dots\dots\dots (2)$$

$$\frac{w_3}{w_1} = \frac{s+d_3}{s-d_3}, \dots\dots\dots (3)$$

From (1), (2), and (3) we get

$$1 = \frac{(s+d_1)(s+d_2)(s+d_3)}{(s-d_1)(s-d_2)(s-d_3)},$$

and finally, by solving the last equation,

$$s = \sqrt{-\frac{d_1 d_2 d_3}{d_1 + d_2 + d_3}}. \dots\dots\dots (4)$$

Three determinations effected by this method, in which  $w_2$  was chosen approximately equal to  $\sqrt{w_1 w_3}$ , gave for  $s$  the values 1118.11, 1118.75, 1118.6 millim.—Wiedemann's *Annalen*, 1882, no. 1, vol. xv. p. 176.

\* See G. Wiedemann, *Galvanismus*, [2] i. p. 254.



## ON THE COMBINATION OF CARBONIC ACID AND WATER.

BY S. WROBLEWSKI.

If carbonic acid be sufficiently compressed in contact with water, in a space kept at zero, the portion of the acid not absorbed liquefies, and two distinctly separate liquids are obtained :—water, more or less saturated, below ; and liquid carbonic acid, lighter, above. The pressure being slowly lessened, the carbonic acid volatilizes, and the whole returns to the original state. But if we compress the carbonic acid almost to liquefaction and then allow the gas to expand a little, so as to produce a trace of solid substance either in the water or on the sides of the tube, the following phenomenon is observed :—Every time that the pressure while being augmented passes through a determined point (which I will call the *critical pressure*), the tube becomes covered with an opaque rime ; and every time the same point is passed through in diminishing the pressure, the rime disappears. The critical point, at zero temperature, is at the pressure of 12·3 atmospheres. The phenomenon can be reproduced at pleasure, if the pressure be not too much diminished, and consequently the ice does not completely disappear. The latter can be preserved as long as we please, if the pressure remains greater than that above indicated.

The phenomenon is likewise produced at higher temperatures than zero. The value of the critical pressure rises with the temperature. At\*

	atm.		atm.		atm.
0·48 it is	12·7	3·6 ....	17·9	6·1 ....	23·3
2·7 ....	16·7	5·3 ....	21·8	6·8 ....	26·1

No such result is obtainable by experimenting with water and air. At zero, with the strongest expansion possible with my apparatus, a little ice is seen to form in the water, which soon melts without producing any rime.

The explanation of the above-described phenomenon appears to me necessarily to involve the existence of a hydrate of carbonic acid, readily dissociable, and capable of being formed by pressure, like M. Ogier's chlorhydrate of phosphuretted hydrogen. The critical pressure would be the dissociation-tension of the formed hydrate. The proportion of water and acid seeming to have no influence on the value of the critical tension, it is probable, from M. Debray's researches, that there is only one hydrate of this acid, containing equal volumes of carbonic acid gas and aqueous vapour. In order that it may readily crystallize, a portion of substance already crystallized must be present ; the expansion of the gas, which determines a local lowering of temperature, serves to produce this effect.—*Comptes Rendus*, Jan. 30, 1882, p. 212.

\* The numbers are the means of the pressures at which the rime begins to disappear and to form.

THE  
LONDON, EDINBURGH, AND DUBLIN  
PHILOSOPHICAL MAGAZINE  
AND  
JOURNAL OF SCIENCE.

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[FIFTH SERIES.]

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APRIL 1882.

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XXVII. *An Examination of Vacua.*  
By J. B. HANNAY, F.R.S.E., F.C.S.\*

[Plate VI.]

THE discovery detailed in a paper read before the Royal Society †, that solids are capable of absorbing and fixing large quantities of gases, led me to an examination of various surfaces in contact with gases. It soon became apparent that not only is there a closely adherent layer of gas on every surface, as shown by Crookes and Liveing and Dewar, but that the gas seems even at ordinary pressures to penetrate into, or combine with, the surface of the glass, and that it is with extreme difficulty that even a portion of this gas is driven off, the greater portion remaining fixed even to the softening-point of the glass. Experiments soon led me to the conclusion that the estimates made as to the real extent of the evacuation of spaces were fallacious; and a serious examination of the extent of evacuation was attempted. There was also in my mind the wish to test, if at all possible, the idea held by Euler, and advocated by Grove and others, that radiation may be propagated by ordinary matter, and not by the luminiferous æther. The idea was, to evacuate a space as perfectly as possible and subject it to intense cold, and then test whether or not it would pass radiant energy. As it was evident that the pressure of mercury vapour is quite appreciable at ordinary temperatures, and is in itself quite sufficient

\* Communicated by the Author.

† Proc. Roy. Soc. No. 214, 1881.

for the propagation of radiation, and as the apparatus would require to be heated to a high temperature, mercury as an evacuating agent was abandoned, and fusible metal substituted. The "barometric height" of fusible metal is about 41 inches, so that all apparatus had to be constructed on that scale.

The fusible metal was composed of 50 per cent. bismuth and 25 per cent. tin and lead respectively; and its fusing-point was  $94^{\circ}$ . Increase of tin or lead raised the fusing-point; but a considerable increase of bismuth (10 per cent.) only raised the fusion-point a few degrees. A variation of 3 per cent. in any of the constituents made little difference. About 30 lb. of the metal was prepared. A portion was heated in a piece of combustion-tubing over the blowpipe, but gave off no perceptible vapours. Pure hydrogen was passed over 20 grms. of the metal in a porcelain boat in a combustion-furnace at a red heat, but after eight hours it had lost only 5 milligrammes, showing that fusible metal is quite fixed, as the empty boat might lose that weight when heated so long. A portion was placed in one end of a piece of combustion-tubing connected with a Sprengel pump, the end containing the metal being slightly elevated. The tube was then evacuated, and the portion away from the metal heated until no more gas was given off, and the McLeod gauge showed an exhaustion of a millionth of an atmosphere. The fusible metal was then gently fused and allowed to run down to the end which had been heated. The blowpipe was again applied and the metal strongly heated; but it gave off no appreciable amount of gas. The metal was therefore held to be free from dissolved gases; and being found to be suitable for the work required of it, an attempt was made to work a Sprengel pump with it. Although its melting-point was  $94^{\circ}$ , it was not thoroughly liquid till  $115^{\circ}$  or thereby; so it was determined to work at a temperature of from  $120^{\circ}$  to  $150^{\circ}$ , to ensure free flow of the metal. After several experiments a bath was constructed as in fig. I. It was made of strong sheet iron with double sides and three sets of windows. Its dimensions are, length of bath 6 ft., length of feet 10 in., inside space 10 in. by 8 in. It had a strong iron tube with four arms running down one side, set in a step at the bottom of the bath, and bolted to the top by a nut, so that it could be removed and the glass apparatus attached for experiment. It was found that, when fitted with a loosely fitting lid, the heat from one of Fletcher's heaters was sufficient when passing from below to maintain the interior at a temperature of  $300^{\circ}$ . The windows were simply pieces of glass made so as to be easily removed to gain access to the interior.

After some preliminary trials the apparatus shown in fig. II. was constructed. The bulb A, which is connected with B by a ground joint, has its lower extremity ground to fit the upper part of the bulb C. D is a tube leading to the mercury Sprengel. E are the bulbs to be evacuated. F is a narrow tube which allows the metal to run very slowly into the pump G. The stopcocks and ground joints were lubricated with Mr. Crookes's invention, burnt india-rubber, which is the only substance of use at high temperatures. I think it acts better at high than at low temperatures, because it soon hardens up on the outside to a hard varnish-like body which is quite impervious to gases. The india-rubber must be the pure variety, such as is used for toy balloons.

The *modus operandi* is as follows :—The apparatus being fixed inside the bath with the joints all made, the stopcocks *a* and *d* are closed and *b* and *c* left open. The ordinary mercury-pump is then set in motion till a good vacuum is obtained. During the evacuation the stopcock *d* is slightly opened, the point being dipped in fusible metal, and the metal allowed to rise till it is just inside *d*, and the cock then closed.

The fusible metal is poured into C through *a*, care being taken to open *a* only very slightly at first. It was found that the fusible metal adheres to the glass, and that no air is admitted with the metal, as would be the case with mercury. When all the metal is in C, the connexion with the Sprengel pump at D is sealed off. The metal is now running very slowly down through F, and acting as a Sprengel pump through G, evacuating the bulbs E. The stopcock *b* is closed, so that the metal collects in B. When B is nearly full the metal is transferred to the top by the following method:—*b* and *c* are opened, transferring the metal from B to A, and then closed, and A disconnected from B; it is then raised and adapted to C, the upper part of which beyond the stopcock *a* is filled with fusible metal. The tube below *d* also being full, no air is allowed to get in; *d* and *a* are then opened, when the metal runs into C. A is now returned to the bottom for a new charge. There is great difficulty in handling the bulbs, owing to the heat, but with flannel and proper clamps the work can be got through. During the evacuation the bulbs E are heated nearly to the softening-point, so as to free them from air; and after an hour or so, B is allowed to fill up full and the metal to pass up into E, sweeping any residual gas into the upper tube H, where it is imprisoned by freezing the metal by a blast of cold air. B is then emptied, and the exhaustion again proceeded with, E again heated

and filled up, and the residual air again imprisoned in H by a new layer of frozen metal. After the first heating the residual gas does not show itself, as the metal goes right up into contact with that formerly frozen there. It seems that if the quantity of gas is very small, it only forms a layer or coating on the glass, and does not form a bubble. This seems to show that the McLeod gauge only measures the excess of residual gas over that required to saturate the glass surface. When sufficient exhaustion was supposed to have been attained, the bulbs E were sealed off; and here it was found that the whole work had been futile, because, on melting the tube through the metal just below the barometric height, in order to detach the bulbs, the appearances shown in figs. III. and IV. were seen. A large amount of gas was given off whenever the glass became soft enough for sealing. Fig. III. shows the sweating of the gas-bubbles when just softening. Fig. IV. shows a tube melted all round for some distance and the large amount of gas driven off. It must be remembered that this tube had been evacuated so far that it gave no residual gas on passing up the metal.

Some further attempts were made to get the bulbs evacuated again, when it was intended to heat the tube at the point of sealing till it was soft previous to sealing, allowing it in fact to be sucked in till it was nearly closed, pumping away the gases, so that none would come off on melting for the final sealing. Experiments showed that when once the glass was melted in a good vacuum no further gas would come off on remelting. It was found, however, that the stopcocks were all leaky, having warped by the long heating (the operation takes a whole day); and after fighting with this form of apparatus, it was abandoned for that shown in fig. V. Here, instead of stopcocks, the tubes were bent round like safety-funnels, and narrowed very much at the bends; and the stopping was effected by a blast of cold air kept blowing on the joint to be closed, and stopping the blast whenever it was required to be opened—the heat of the bath remelting the frozen plug. The transference of the metal from bottom to top was effected as in the other apparatus. In this the bulbs E were connected with the Sprengel pump by HD, but were afterwards separated by passing metal up into H, sweeping out residual air and freezing it in H, before the final evacuation with the fusible metal was begun. This form was adopted in order that the residual air might be subjected to no pressure, but have a free space to pass out into, thus avoiding condensation on the glass. Some progress



was made with this method; but a new difficulty arose. The fusible metal expands very much after solidification, and often bursts the tube containing it; in fact it always bursts it if allowed to cool far enough; but, as its principal expansion-point is  $35^{\circ}$ , or  $60^{\circ}$  below its freezing-point, it was hoped that by keeping the temperature between  $50^{\circ}$  and  $70^{\circ}$  a good stoppage would be obtained. I may mention that the expansion of the metal at  $35^{\circ}$  is so great that, if allowed to solidify in a common deep goblet, it invariably splits it; but it may be allowed to cool and solidify in a shallow stew-pan with safety. After working for some weeks in vain attempts to regulate the temperature of the stoppers, the difficulty was found to be so great that (some point being momentarily overlooked) the apparatus was invariably broken. When it is remembered that working at such high temperatures the glass often cracks, being extremely brittle and having little tenacity, it will be understood that failures were often due to this cause; but when something had gone wrong, and I could not get the metal out without cooling the apparatus, I have often had to stand by and see two days' glass-blowing slowly disintegrated without being able to save a tube.

It became manifest that frozen stoppers would not do, at least where many were required, and stopcocks were not reliable when in communication with the vacuum; so a new apparatus was constructed, where the stopcocks were under pressure, and therefore not liable to leakage, and where leakage could only take place to the unimportant side of the apparatus. The pumping action was also abandoned, and the apparatus shown at fig. VI. used. The tube A was attached to a mercury-pump, and the cocks *a*, *b*, and *c* closed. When evacuating, *b* was slightly opened, and dipped into a pot of metal so that it filled up to the inside of the stopcock, which was then closed. When a good vacuum had been obtained, the tubes B and C were heated and allowed to be sucked in till nearly closed. The same was done with the tubes above and below the bulbs E; and they were also heated nearly to the softening-point. B was then sealed off, and the metal poured through F into D till nearly full, and C then also sealed off from the Sprengel pump. Some metal was left in F, and new burnt india-rubber applied to *a*.

The bulbs E were then strongly heated and *c* opened, so that the metal rose and swept the residual air into H, where it was frozen by cold air. No leakage can take place by *b* or *c*, as they are under more than an atmosphere of pressure, while leakage by *a* is of little consequence, but seldom occurred. The tube at the bottom of D was frozen by the same blast as was

used for H. *c* and *b* are now opened, and the metal run out of E, which is again heated, and new metal passed round from D, which holds sufficient metal for six fillings of E. The residual air, if there is any, is always imprisoned by a new layer of frozen metal in H. The bulbs were then sealed off; but even after all this treatment, a little air was seen to come off when quite melted. The best evacuation obtained in this way was tested as follows. One bulb was placed in a freezing-mixture of calcium chloride and snow, and the other interposed between a standard candle and radiometer kindly lent me by Sir W. Thomson; but no retarding effect further than that due to the glass was observed, as on admitting air to the bulbs no acceleration took place.

It was found that, by increasing the proportion of lead in the alloy by 20 per cent., the expansion on solidification was greatly reduced, and enabled the freezing method of stoppage to be used: this raised the melting-point to  $108^{\circ}$ . The last apparatus was now modified, so as to dispense with stopcocks, and a new attempt made. The bulbs were also reconstructed for testing the conducting-power of the vacuum for electricity, one bulb being made as shown in fig. VII. In this the platinum wires were led into cups filled with fusible metal, so that no leakage along the platinum wire was possible. Wires were led into the cups from the outside, insulated with asbestos and shellac, and the spark from a strong Holtz machine made to pass. At the highest exhaustion obtained by the Sprengel pump,  $\frac{1}{23,000,000}$  of an atmosphere measured by the McLeod gauge, the spark passed as a flash illuminating the glass surface inside; but on exhausting as above with fusible metal, no power I could obtain would cause a spark to pass through the vacuum. A Leyden battery of 12 jars was tried, and a coil giving a 12-inch spark, but with no effect. Mercury vapour seems, therefore, to conduct the spark. An attempt was made to detach the bulbs, but they were fractured. It was found that it was by no means necessary to keep the fusible metal in a vacuum, as it dissolves no gases; and as the great length of the apparatus rendered its construction troublesome and its fracture easy, a new apparatus was made as shown in fig. VIII.

This was constructed to obtain a simple torricellian vacuum, a movable iron bucket below being provided, so that the metal could be raised and lowered. The tube, from the bulbs downwards, was 48 inches long; and the lower end was turned into a spiral, with the termination turned inside the spiral, so that the end could nowhere touch the tube. I need not describe

the treatment, as it was similar to that before employed. The vacuum obtained by this method would not pass a spark. The metal used in this experiment had extra lead added to it, so that it could be frozen.

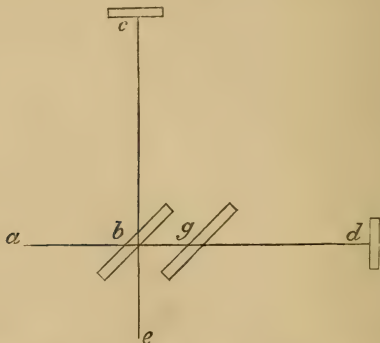
The bulbs were detached in the following way. The metal was passed up for the last time and frozen, and the tube melted through the metal at *a*, leaving a good column of frozen metal between the bulbs and the seal, so that any gas given off could not get into the former. The metal was then lowered out of the bulbs, and again frozen above *b*, where the tube was again melted through, and the air given off kept imprisoned by the solid metal above *b*. This vacuum was tested by the radiometer, but gave no retardation beyond that due to the glass; it would not, however, conduct a spark. To test whether the glass had been really freed from gas by this process, a pair of bulbs were evacuated as before, and the metal passed fully half up the upper one. The bulb was then heated to softening, so that its sides were sucked in in several places just below the surface of the metal; and it was invariably found that a sweat of gas-bubbles was formed between the glass and the metal, showing that the glass still retained air. The only method by which a real vacuum might be obtained (putting aside glass vapour), would be by having the bulbs made of hard glass outside and soft glass inside, so that the inside might be fused and its gas layer driven off, without collapsing the bulbs; but I am not sufficiently skilled in glass-blowing to make such bulbs. As I have been unable to get them made, the experiment has not been tried.

The work, as far as it goes, shows that no conclusions can be drawn as to the nature of properties of high vacua, after such vacuous space has been cut off, by sealing one of the tubes by fusion; and it is doubtful whether the measurements by the McLeod gauge represent the true density of the residual atmosphere. The object of this investigation—the testing of Euler's hypothesis—has not been fulfilled, although nearly six months' work was spent upon it, the accidental breakages making the testing of a method a matter of a month's work. I must record my hearty thanks to my two assistants, Messrs. Campell and McConechy, for the unwearied aid they have given me in this troublesome investigation.

XXVIII. *Interference Phenomena in a new Form of Refractometer.* By ALBERT A. MICHELSON\*.

IN an experiment undertaken with a view to detecting the relative motion of the earth and the luminiferous æther ('American Journal of Science,' No. 128, vol. xxii.), it was necessary to produce interference of two pencils of light which had traversed paths at right angles with each other. This was accomplished as follows:—The light from a lamp at *a* (fig. 1)

Fig. 1.



was separated into two pencils at right angles, *bc* and *bd*, by the plane-parallel glass *b*; and these two pencils were returned to *b* by the mirrors *c* and *d*, whence they coincide along *be*, where they are viewed by a small telescope at *e*. It is evident that, so far as the interference is concerned, the apparatus may be replaced by a film of air whose thickness is *bc*—*bd*, and whose angle is that formed by the image of *d* in *b*, with *e*.

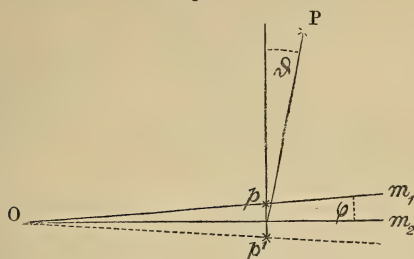
The problem of interference in thin films has been studied by Feussner; but his equations do not appear to give the explanation of the phenomena observed. In particular, in the *Annalen der Physik und Chemie*, No. 12, 1881, on page 558, the conclusion drawn from the preceding equations is that the interference-fringes are straight lines; whereas in the above apparatus they are in general curves, and there is but one case—that of the central fringe in white light—which is straight.

I have therefore thought it worth while to attempt the solution of the problem for a film of air for small angles of incidence, and neglecting successive reflections (which in the

\* Communicated by the Author.

above-described instrument do not exist); and though the solution is not perhaps adapted to the general problem, it accounts satisfactorily for all the phenomena observed in the special case. Let  $O m_1 O m_2$  (fig. 2) be two plane mirrors

Fig. 2.



whose intersection is projected at  $O$ , and whose mutual inclination is  $\phi$ . The illumination at any point  $P$  (not necessarily in the plane of the figure) will depend on the mean difference of phase of all the pairs of rays starting from the source and reaching  $P$ , after reflection from the mirrors—a pair of rays signifying two rays which have started from the same point of the source.

If the area of the luminous surface is sufficiently large, the illumination at  $P$  will be independent of the distance, form, or position of the surface. Suppose, therefore, that the luminous surface coincides with the surface  $O m_1$ . Its image in  $O m_1$  will also coincide with  $O m_1$ ; and its image in  $O m_2$  will be a plane surface symmetrical with  $O m_1$  with respect to  $O m_2$ ; and for every point  $p$  of the first image, there is a corresponding point  $p'$  of the second, symmetrically placed and in the same phase of vibration. Suppressing, now, the source of light and the mirrors, and replacing them by the images, the effect on any point  $P$  is unaltered. Consider now a pair of points  $p, p'$ . Let  $S$  be the angle formed by the line joining  $P$  and  $p$  (or  $p'$ ) with the normal to the surface,  $S$  and  $\phi$  being both supposed small,

$$\Delta = Pp' - Pp = pp' \cdot \cos S.$$

The difference between this value of  $\Delta$  and the true value is  $2Pp \cdot \sin^2 \frac{\psi}{2}$ , where  $\psi$  is the angle subtended by  $pp'$  at  $P$ . If  $S$  is a small quantity,  $\psi$  is a small quantity of the second





It is proposed to find such a distance  $P$  that, with a given aperture, these differences shall be as small as possible, which is equivalent to finding the distance from the mirrors at which the phenomena of interference are most distinct.

The change of  $\Delta$  for a change in  $\theta$  is

$$\frac{\partial \Delta}{\partial \theta} = - \frac{2(t_0 + P \tan \phi \tan i) \frac{\tan \theta}{\cos^2 \theta}}{(1 + \tan^2 i + \tan^2 \theta)^{\frac{3}{2}}}. \quad (2)$$

The change of  $\Delta$  for a change of  $i$  is

$$\frac{\partial \Delta}{\partial i} = 2 \frac{(1 + \tan^2 i + \tan^2 \theta) \frac{P \tan \phi}{\cos^2 i} - (t_0 + P \tan \phi \tan i) \frac{\tan i}{\cos^2 i}}{(1 + \tan^2 i + \tan^2 \theta)^{\frac{3}{2}}}. \quad (3)$$

For  $\frac{\partial \Delta}{\partial \theta} = 0$  we have  $\theta = 0$  (or  $\Delta = 0$ ).

For  $\frac{\partial \Delta}{\partial i} = 0$  we have

$$(1 + \tan^2 i + \tan^2 \theta) P \tan \phi = (t_0 + P \tan \phi \tan i) \tan i,$$

or

$$(1 + \tan^2 \theta) P \tan \phi = t_0 \tan i,$$

whence

$$P = \frac{t_0}{\tan \phi} \tan i \cos^2 \theta.$$

Hence the fringes will be most distinct when  $\theta = 0$  and

$$P = \frac{t_0}{\tan \phi} \tan i. \quad (4)$$

This condition coincides nearly with that found by Feussner.

If the thickness of the film is zero, or if the angle of incidence is zero, the fringes are formed at the surface of the mirrors. If the film is of uniform thickness, the fringes appear at infinity. If at the same time  $\phi = 0$  and  $t_0 = 0$ , or  $\phi = 0$  and  $i = 0$ , the position of the fringes is indeterminate. If  $i$  and  $\phi$  have the same sign, the fringes appear in front of the mirrors; if  $i$  and  $\phi$  have opposite signs, the fringes appear behind the mirrors.

To find the form of the curves as viewed by the eye at  $E$ , call  $T$  the distance between the surfaces at  $E'$ , the projection of  $E$ . From  $P$  draw  $PR$  parallel to  $DP'$ , and  $RS$  parallel to  $CP'$ , let  $RS = c$ , and let  $SE = D$ . We have then  $t_0 = T + c \tan \phi$ , whence, since  $c = D \tan i$ ,

$$\Delta = 2 \frac{T + (D + P) \tan \phi \tan i}{\sqrt{1 + \tan^2 i + \tan^2 \theta}}. \quad (5)$$

If, on a plane perpendicular to  $EE'$  at distance  $D$  from  $E$ , we call  $x$  distances parallel to  $P'C$ , and  $y$  distances parallel to  $P'D$ , counted from the projection of  $E$  on this plane, then, putting  $\tan \phi = K$  and  $D + P = S$ , we have for the equation to the curves,

$$\Delta = 2 \frac{DT + SKx}{\sqrt{D^2 + x^2 + y^2}},$$

or

$$\Delta^2 y^2 = (4S^2 K^2 - \Delta^2) x^2 + 8TSKDx + (4T^2 - \Delta^2) D^2. \quad (6)$$

If, numerically,

$\Delta < 2SK$ ,	the curve is a	hyperbola.
$\Delta = 2SK$ ,	" "	parabola.
$\Delta > 2SK$ ,	" "	ellipse.
$K = 0$ ,	" "	circle.
$\Delta = 0$ ,	" "	straight line.

All the deductions from equations (4) and (6) have been approximately verified by experiment.

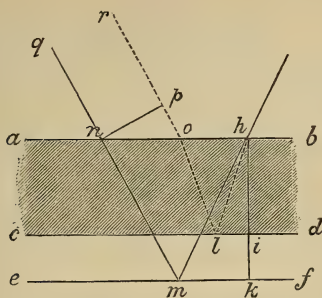
It is to be noticed that in the most important case, and that most likely to occur in practice, namely that of the central fringe in white light, we have  $\Delta = 0$ , and therefore also  $t_0 = 0$ ; and in this case the central fringe is a straight line formed on the surface of the mirrors. Practically, however, it is impossible to obtain a perfectly straight line; for the surface of the mirrors is never perfect.

It is also to be noticed that the central fringe is black; for one of the pencils has experienced an external, the other an internal reflection from the surface of  $b$  (fig. 1). This will not, however, be true unless the plate  $g$  (which is employed to compensate the effect of the plate  $b$ ) is of exactly the same thickness as  $b$  and placed parallel with  $b$ . When these conditions are not fulfilled, the true result is masked by the effect of "achromatism" investigated by Cornu (*Comptes Rendus*, t. xciii. Nov. 21, 1881). This remark leads naturally to the investigation of the effect of a plate of glass with plane parallel surfaces, interposed in the path of one of the pencils.

The effect is independent of the position of the glass plate, provided its surface is kept parallel with the corresponding mirror. Suppose, therefore, that it is in contact with the latter, and let  $cd$  (fig. 4) represent the common surface. Let  $t = hi$  = thickness of the glass,  $i$  = angle of incidence,  $r$  = angle of refraction,  $n$  = index of refraction,  $\lambda$  = wave-length of light. Let  $ef$  represent the image of the other mirror, and put  $n_0 = \frac{hk}{t}$ .

It can readily be demonstrated that the path of the rays in the instrument is equivalent to that given in the figure, where

Fig. 4.



one of the rays follows the path  $qnmh$ , and the other the path  $rolh$ . Suppose the mirrors  $cd$  and  $ef$  parallel. Then, as has been previously shown, the curves of interference are concentric circles formed at an infinite distance. Therefore the rays  $qn$ ,  $ro$ , whose path is to be traced, are parallel, and from the point  $h$  they coincide. Their difference of path is

$$2nm - 2hl - op;$$

and their difference of phase is

$$\begin{aligned} \phi &= \frac{2nm}{\lambda} - \frac{2hl}{\lambda} - \frac{op}{\lambda} \\ &= \frac{2n_0 \cdot t}{\lambda \cos i} - \frac{2n \cdot t}{\lambda \cos r} - \frac{2t}{\lambda} (n_0 \tan i - \tan r) \sin i; \end{aligned}$$

whence

$$\phi = \frac{2t}{\lambda} [n_0 \cos i - n \cos r]. \quad \dots \dots \dots (7)$$

Let it be proposed to find the value of  $n_0$  which renders any particular ring achromatic. The condition of achromatism, according to Cornu, is

$$\frac{d\phi}{d\lambda} = 0,$$

which gives

$$\phi + 2t \left( \cos r \frac{dn}{d\lambda} - n \sin r \frac{dr}{dn} \cdot \frac{dn}{d\lambda} \right) = 0.$$

We have

$$n = \frac{\sin i}{\sin r},$$

whence

$$\frac{dr}{dn} = - \frac{\sin^2 r}{\sin i \cos r},$$

whence

$$\phi + \frac{2t}{\cos r} \cdot \frac{dn}{d\lambda} = 0.$$

By Cauchy's formula we have

$$n = \alpha_1 + \frac{\alpha_2}{\lambda^2},$$

whence

$$\frac{dn}{d\lambda} = - \frac{2\alpha_2}{\lambda^3}.$$

Substituting, we have

$$n_0 \cos i - n \cos r = \frac{2\alpha_2}{\lambda^2 \cos r} \approx \frac{2\alpha_2 + n \cos^2 r}{\cos i \cos r};$$

or, finally,

$$n_0 = \frac{2(n - \alpha_1) + n \cos^2 r}{\cos i \cos r}. \quad \dots \dots \dots (8)$$

If the angle  $i$  is small, the value of  $n_0$  will vary very little with  $i$ ; consequently there will be a large number of circles, all nearly achromatized. Under favourable circumstances as many as one hundred rings have been counted, using an ordinary lamp as source of light.

The difference of path of the two pencils which produce these rings in white light may exceed a thousand wave-lengths.

XXIX. *On the Refractive Index and Specific Inductive Capacity of Transparent Insulating Media.* By J. HOPKINSON, D.Sc., F.R.S.\*

ONE of the deductions from Maxwell's electromagnetic theory of light is, that the specific inductive capacity of a medium is equal to the square of its refractive index. Another deduction is, that a body which is opaque to light, or, more generally, to radiant energy, should be a conductor of electricity. The first deduction appeared so clear an issue that many experimenters have put it to the test. The results

\* Communicated by the Physical Society, having been read at the Meeting on February 25, 1882.



may be briefly summarized thus:—Some bodies (such, for example, as hydrocarbon oils\* and paraffin-wax) agree with Maxwell's law so well that the coincidence cannot be attributed to chance, but certainly points to an element of truth in the theory: on the other hand, some bodies, such as glass† of various kinds, fluor-spar‡, Iceland spar‡, and the animal and vegetable oils§, have specific inductive capacities much greater than is indicated by their refractive indices.

How do these latter results really bear on Maxwell's theory? The facts are these. Taking the case of one substance as typical, the refractive indices of light flint-glass are very accurately known, the period of disturbance ranging from  $\frac{1}{4.0 \times 10^{14}}$  second to  $\frac{1}{7.6 \times 10^{14}}$  second; the specific inductive capacity is

known to be about 6.7, the time of electrical disturbance being from  $\frac{1}{17000}$  second to a few seconds. If from the observed refractive indices we deduce by a formula of extrapolation the refractive index for very long waves, we find that its square is about one third of 6.7. There can be no question about the accuracy of the observed refractive indices; and I have myself no doubt about the specific inductive capacity; but formulæ of extrapolation are always dangerous when used far from the actual observations. If Maxwell's theory is true, light flint-glass should be perfectly transparent to radiations having a wave-period of, let us say,  $\frac{1}{17000}$  second; because this glass is sensibly a perfect electrical insulator, its refractive index for such waves should be about 2.6. Are there any facts to induce us to think such a thing possible? It is well known that in some cases strong selective absorption of light in the visible spectrum causes what is known as anomalous dispersion; that is to say, the body which presents such selective absorption of certain rays has a refractive index abnormally low for waves a little shorter than those absorbed, and an index abnormally high for waves a little longer than those absorbed||.

Light flint-glass is very transparent through the whole visible spectrum, but it is by no means transparent in the infra-red. If the absorption in the infra-red causes in light flint-glass anomalous dispersion, we should find a diminished refrac-

\* Silow, *Pogg. Ann.* 1875, p. 382; 1876, p. 306. Hopkinson, *Phil. Trans.* 1881, part i. p. 371.

† 'Cavendish Researches,' edited by Clark Maxwell; Schiller, *Pogg. Ann.* 1874, p. 535; Wullner, *Sitz. k. bayer. Akad.* 1877, p. 1; Hopkinson, *Phil. Trans.* 1878, part i., 1881, part ii.

‡ Romich and Nowak, *Wiener Sitz. Bd.* lxx. part 2, p. 380.

§ Hopkinson, *Phil. Trans.* 1881, part ii.

|| 'Theory of Sound,' by Lord Rayleigh, vol. i. p. 125.

tive index in the red. We may say that we have a hint of this; for if we represent the refractive indices by the ordinates of a curve in which the squares of the reciprocals of the wave-lengths are abscissæ, this curve presents a point of inflection\*. In the part corresponding to short waves it is concave upwards; in the part corresponding to long waves it is concave downwards: the curvature, however, is very slight. Does it not seem possible, looking at the matter from the purely optical point of view, that if we could examine the spectrum below the absorption in the infra-red, we should find the effect of anomalous dispersion, and that the refractive index of such long waves might even be so high as 2.6? To test this experimentally in a conclusive manner would probably not be easy. Perhaps the best chance of finding how these long waves are refracted would be to experiment on the rays from a thermopile to a freezing-mixture. Without an actual measurement of a refractive index below all strong absorption, it cannot be said that experiment is in contradiction to the Electromagnetic Theory of Light; for a strong absorption introduces a discontinuity into the spectrum which forbids us from using results on one side of that discontinuity to infer what they would be on the other side.

XXX. *Water-pipes that do not burst with Frost.* By C. VERNON BOYS, *Demonstrator of Physics, Normal School of Science, South Kensington*†.

**D**URING the severe weather of last winter, Mr. L. S. Powell proposed to me a scheme for preventing the possibility of water-pipes bursting through frost; and I have since learnt that Mr. Mangnall, of Manchester, independently hit upon the same idea. As far as I can remember, there were some letters in the 'Times' describing the use of india-rubber pipes containing air inserted in the service-pipes. This would obviously prevent pipes from bursting; for the pressure is of a nature that is relieved by a comparatively small expansion; and this the india-rubber tube allows to take place in the surrounding water when it collapses. There is, however, one serious objection to this, which is the possibility of the detachment of one end of the flexible tube, in which case a rush of water might cause it to accumulate in one place and obstruct the passage.

\* Proceedings of Royal Society, 1877.

† Communicated by the Physical Society, having been read at the Meeting on November 12, 1881.

Mr. Powell's plan is to make the piping elliptical—either before it is laid, in which case it may be made of that form originally or by passing round pipe through rollers, or afterwards, when suitable hand-squeezers will effect the result without the necessity of removal. As will afterwards be seen, it is not necessary that the pipe should be elliptical throughout; if left round under staples and in other inaccessible places, the adjacent elliptical portions ensure safety. The principle, of course, is obvious. As is well known, the Bourdon pressure-gauge depends on the fact that the area of an elliptical pipe is less than that of a circle of equal perimeter: therefore during increased pressure its section becomes more circular; increased circularity of section produces diminished curvature in the form of the pipe; and so the movements of the end of the pipe are used to measure pressure. Thin brass is used for this purpose, and is so elastic that it returns to its original form when the pressure is removed; and so an indefinite number of increments and decrements of pressure may be measured by it. The case of the elliptical water-piping is different. Here there is not a definite pressure to withstand, but a definite increase of volume; and, moreover, if this increase of volume is resisted, a practically infinite force arises to break down the resistance. The question then is, how best to allow of this increase of volume. The method of the indiarubber pipes I have already mentioned. The other plan is to make them of an elliptical or other-than-round section. There is, however, far more in this suggestion than one would be likely to see at first. Consider the case of a round pipe in which water is beginning to freeze. Increase of volume must take place somewhere. No pipe can be absolutely uniform in strength everywhere. So wherever a place occurs which happens to be a little weaker than the rest, no matter how little, that place will stretch, and necessarily stretch more than other places. But when a round pipe stretches, two things happen—its diameter increases and its thickness decreases; therefore, as the strength of a tube to resist bursting is inversely as the diameter and directly as the thickness, each of these effects makes the stretched portion still weaker than the neighbouring parts; therefore a round pipe under the action of frost is in a state of unstable equilibrium; the consequence is, knobs form on the pipe, and ultimately burst.

Now consider the case of an elliptical pipe, of such strength, of course, as to stand the ordinary water-pressure. As before, suppose some portions are weaker than others. When expansion takes place they will suffer most, and will begin to give way. But an elliptical pipe on giving becomes more circular,

*and this the more easily as its section departs more from the circle*; so the very fact of its becoming more circular makes it less ready to change its form. In a very little while, therefore, though originally weaker, it will become as strong as neighbouring portions: therefore an elliptical pipe under the action of frost is in a state of stable equilibrium, and, instead of giving way in the bulbous manner of a circular pipe, it uniformly becomes more circular. Now the expansion of water in becoming ice is known; and therefore it is easy to calculate by compound interest how many *complete* freezings (that is, freezings from one end of the pipe to the other) any given section of piping will stand before it becomes round. Of course, in practice, the whole length of a pipe does not get frozen; yet if it were originally all of it elliptical, the unfrozen portions would be effective in preventing the more exposed parts from bursting; because as soon as the exposed portions have become rounder than the rest, the latter, and not the former, will yield. If two places in the pipe become completely frozen through and then the intermediate portion freezes, it is true that parts beyond the frozen plug will have no effect.

Mr. Powell and I tried a series of experiments on the subject to see if, in practice, the pipes behaved as we expected. We obtained a quantity of  $\frac{3}{4}$ -inch lead pipe, about  $\frac{1}{10}$  inch thick, and some thin composition pipe of the same size. The piping was cut into lengths of about three feet; half of them were squeezed into an approximately elliptical form, and the rest left circular in section. The degree of ellipticity was such that the major axis was a little more than twice the minor axis. One end of each pipe was squeezed together and soldered. Into the other ends brass plugs cut with a sharp thread were screwed while hot, having been previously smeared with a cement of rosin, beeswax, and red-ochre. After these plugs were inserted and while still hot, the lead was, as an additional precaution, squeezed over a narrower portion of the plug above the screw-thread. In each plug a hole had been drilled and tapped. Through these holes the pipes were filled with water; and then iron screws, with washers of leather boiled in beeswax and tallow, were used to make a tight joint. The pipes were then all laid together in a long box, and surrounded with a freezing-mixture. When a short test-pipe of the same diameter showed that the water was completely frozen, the pipes were removed and thawed. The round composition pipe was burst. The round lead pipe was swollen in an irregular manner. The elliptical piping had become slightly rounder, but was perfectly uniform in shape from end to end, which

was not the case when it was put in the freezing-mixture. The most noticeable thing, however, was the fact that all the unburst pipes had become good water-hammers, and this showed that leakage could not have occurred. The screws were removed, the pipes filled, again screwed up and refrozen, and this was repeated till all were burst. The round lead and the thin elliptical composition pipe burst at the third freezing, and the elliptical lead pipe at the sixth. Judging from the fact that it required three freezings to burst the round pipe, one might be led to suppose that a round pipe would last equally long under ordinary conditions, which is certainly not the case. The reason is that, under ordinary conditions, a greater length freezes at a time and more slowly; and a slight inequality arising, the expansion from a greater volume of water is concentrated on the weaker places, which therefore give way during the second, if not the first, freezing of the water.

It might be thought that, as the outer layers of ice are below the freezing-point when the pipe is being cooled, they would not act as a plastic body and accommodate themselves to the changing form of the pipe; but no doubt can remain as to their behaviour in this respect when the pipe is cooled in air; for in the freezing-mixture, where the rate of cooling must be much more rapid, such accommodation takes place perfectly, even thin composition pipes changing their form and becoming round. The apparent plasticity of the ice may depend on fracture and regelation; for if the outer layers are below the freezing-point, and a bursting-pressure is brought to bear on the compound pipe formed of lead and ice, it might yield, the lead bending and the ice cracking, and so allowing the water to penetrate the cracks and freeze in them. Whether this action takes place or not does not much matter: the result, as in the somewhat different case of glacier-motion, is much the same.

If the pipe is made of such a form that it will not become round till it has been completely frozen, say, three times, it will take a great many frosts to burst it, as those parts that do not freeze easily will protect the more exposed portions; so absolute security may be relied upon till ordinary round pipes have burst once or twice; and then the now nearly round ones may be squeezed back to their original form. The choice, then, is between two evils; either burst pipes, with the usual damage and cost of repair, or the trouble of inspection every second or third time that the neighbours find that the "thaw" has burst theirs.

We thought it possible that iron might be sufficiently elastic



to return to its original form; and so we froze water in two  $\frac{3}{4}$ -inch iron gas-pipes, one round and one which had been flattened when red-hot. The round pipe burst the first time; the flat one did return slightly when thawed, but not enough to prevent its bursting during the second operation.

No doubt most people will not consider this proposal of Mr. Powell's a satisfactory cure for burst pipes; they would like something which could be fixed in their houses and which would be always safe without further attention. But till such a discovery is made, I think elliptical pipes give the best solution of a problem which has troubled every householder.

As the subject of this paper is of physical as well as general interest, I hope that it may be considered not unworthy of the attention of the Physical Society.

XXXI. *Electro-optic Experiments on various Liquids.* By JOHN KERR, LL.D., *Free Church Training College, Glasgow.*

[Concluded from p. 169.]

*Sulphides,  $(C_nH_{2n+1})_2S$ .*

13. **T**HESE are purely negative, and rise in power as  $n$  increases; they are weaker than the corresponding oxides, but much stronger than the hydroxides.

*Ethyl sulphide*, not a clean liquid, required the jar and 10 to 20 turns of the plate. The effect was purely negative, strengthened by compression parallel to lines of force, and extinguished by tension.

*Butyl sulphide*, tried as a nonconductor, gave a very faint effect, which was barely characterizable as negative. Tried then as a conductor, with increasing charges of the jar, it gave a set of brilliant effects, always purely negative.

*Amyl sulphide*, a feeble photogyre, hardly separating the red and blue at extinction, was rather stronger than the last. It acted well as a nonconductor, giving a clear effect which was purely negative. As a conductor, with increasing charges, it gave increasingly brilliant effects, always negative by both tests.

*Ethyl disulphide* was also examined, and was found to be purely negative, like the protosulphide, but much stronger. As a nonconductor it gave a pure and moderately strong effect; and as a conductor, with increasing charges of the jar, it gave a fine series of restorations, all purely negative, extinguished perfectly by tension parallel to lines of force.

*Mercaptans,  $C_nH_{2n+1}HS$ .*

14. These are purely positive, and rise in power as  $n$  increases ; they are stronger than the corresponding fatty acids.

*Ethyl hydrosulphide* acted very well in the plate cell as a conductor, without the jar. The effect from extinction was not very faint, and was slow enough to be characterized as purely positive.

*Butyl hydrosulphide* is distinctly stronger. As a nonconductor, it gave a faint but clear effect, which was purely positive ; and as a conductor, with increasing charges of the jar, it gave a set of increasingly brilliant effects, which were all strengthened by tension parallel to lines of force, and all weakened to perfect extinction by the proper compression.

*Amyl hydrosulphide*, not a clean sample, acted very like the last, but was rather stronger. As a nonconductor (spark  $\frac{1}{4}$  inch) it gave a good though faint effect, which was purely positive ; and as a conductor, with moderate charges of the jar, it gave an intense restoration, which was always extinguished perfectly by the proper compression parallel to lines of force.

*Formates,  $CH(C_nH_{2n+1})O_2$ .*

15. These are active only as conductors, and certainly positive ; but the effects are faint and impure, the flame restored in the polariscope being distorted and streaky. This form of disturbance was noticed already, though in a milder form, in the allyl and ethylene alcohols.

*Methyl formate*, with moderate charges of the jar, gave an effect which was faint and not at all pure, but certainly positive, strengthened by tension parallel to lines of force, and not sensibly affected by compression.

*Ethyl formate*, with good charges of the jar, acted rather better. The effect was strengthened by tension parallel to lines of force, and much weakened by compression.

*Amyl formate* acted very like the other two. With moderate charges, the effect was pretty strong and distinctly positive, strengthened by tension, and either weakened or not affected by compression. When the discharges were intense, the disturbance masked the regular effect completely.

*Acetates,  $C_2H_3(C_nH_{2n+1})O_2$ .*

16. These are distinctly positive, and otherwise like the formates ; but the effects are purer.

*Methyl acetate* required the jar. With moderate charges the effect was very abrupt but certainly positive, strengthened

by tension, and not affected by compression. The Ruhmkorff-discharges gave afterwards an effect which was more purely positive, weakened regularly by compression; but the liquid was now very much disturbed, and there was a large heat-effect after a few discharges.

*Ethyl acetate* acted hardly so well as the last. With moderate charges of the jar, there was a large deformation of the flame, and the regular effect was very faint, not seizable indeed without the hand compensator; but it was clearly positive, strengthened by tension, and darkened by compression.

*Butyl acetate* acted much better. As a conductor, without the jar, it gave a clear effect which was purely positive by both tests; and with these feeble discharges the disturbance of the flame was hardly noticed.

*Amyl acetate* acted still better, but not without the jar. With moderate charges it gave a good effect, which was purely positive, strengthened by tension, and extinguished by compression. With strong discharges the effect was still very fine, and purely positive by both tests, the deformation of the flame being hardly sensible.

*Butyrates*,  $C_4H_7(C_nH_{2n+1})O_2$ .

17. The regular effects in these compounds are purely positive and undisturbed, much stronger and finer than in the acetates.

*Methyl butyrate* acted well as a conductor, with or without the jar, giving a series of fine effects with increasing charges, and without any apparent disturbance. The effect, weak or strong, was purely positive, extinguished always by the proper compression parallel to lines of force.

*Ethyl butyrate*, an impure sample, was hardly so strong as the last, requiring the jar and five or more turns of the plate. With good charges the effect was strong, and purely positive by both tests.

*Ethyl isobutyrate* was much stronger, acting well as a non-conductor, and reminding me of the weaker hydrocarbons, amylene &c. With strong charges of the jar it gave a strong, slow, and very fine effect, purely positive by both tests, and without sensible disturbance.

*Isobutyl isobutyrate* gave a fine and purely positive effect as a nonconductor. There was no sensible disturbance even when the electric force was strongest. The action improved evidently for a time as the experiment proceeded, and appeared to be at last as strong as that of benzol.

*Valerates*,  $C_5H_9(C_nH_{2n+1})O_2$ .

18. These are clearly positive, acting better than the acetates, but not so well as the butyrates.

*Methyl valerate*, with strong charges of the jar, gave a faint effect which was distinctly positive, strengthened by tension, and weakened by compression. The effect was very impure, the flame being much deformed.

*Ethyl valerate* was much stronger, and its action was almost perfectly pure. As a nonconductor, it gave a clear, but very faint, restoration from extinction. As a conductor, with increasing charges, it gave a series of fine effects, all purely positive, strengthened by tension, and extinguished by compression.

*Amyl valerate*, a much stronger photogyre than either of the other two, acted only as a conductor, and required the jar. The regular effect, not strong in any case, was always purely positive by both tests.

*Benzoates*,  $C_7H_5(C_nH_{2n+1})O_2$ .

19. These are purely positive, and about as strong as the butyrates.

*Methyl benzoate* acted clearly as a conductor; but the effect without the jar was too abrupt to be characterized. With small charges of the jar the effect was positive by one test, strengthened by tension, and either weakened or not sensibly affected by compression.

*Ethyl benzoate*, as a nonconductor, gave a faint but very good restoration, which was purely positive. Tried then as a conductor, with and without the jar, it gave an intense and very slow effect, always purely positive by both tests.

*Amyl benzoate*, not a clean sample, acted only as a conductor. With moderate charges of the jar, it gave an intense and slow effect which was always purely positive, the extinction-bands being brought in very finely by compression parallel to lines of force.

*Nitrates*,  $C_nH_{2n+1}NO_3$ .

20. These are weak insulators in comparison with most of the preceding ethers: they are clearly but not very purely positive.

*Ethyl nitrate* as a conductor, without the jar, gave a restoration which was distinct, but very faint and abrupt. With moderate charges of the jar, the effect was seen to be positive, strengthened by tension, but not affected by compression. With strong charges the effect was still very abrupt, neither pure nor very strong, but certainly positive.

*Butyl nitrate* is stronger, giving a sure trace of effect as a nonconductor. Tried as a conductor, with moderate charges of the jar, it gave a strong restoration which was certainly positive, strengthened by tension, but not affected by compression. With very strong charges the effect was brilliant, but still too abrupt, being absolutely unaffected by compression parallel to lines of force ; but the contrast between the effects of tension and compression was always perfectly clear.

*Amyl nitrate*, a feeble photogyre, is very like the last, certainly, but not quite purely, positive. With strongest charges of the jar, the effect was still unmanageably abrupt for the second test ; and the liquid was sensibly disturbed.

#### *Nitrites*, $C_nH_{2n+1}NO_2$ .

21. *Ethyl nitrite* was in solution (10 p. c.), and, when tried with strong charges of the jar, gave a very faint effect which was apparently positive.

*Amyl nitrite* acted well with moderate charges of the jar. Although the liquid was disturbed sensibly by discharge, the regular effect was seen to be certainly positive, strengthened by tension, and either weakened or not affected by compression.

#### *Other compounds of C, H, O.*

22. *Aldehyd*,  $C_2H_4O$ , is negative, and hardly so strong as ethyl alcohol. With Ruhmkorff-discharges, and with precautions against permanent heat-effects, it gave a good restoration, regular though very faint, which was clearly strengthened by compression but not by tension.

*Acetone*,  $C_3H_6O$ , is stronger than the last, clearly positive, but a very feeble insulator. With good charges of the jar it gave a clear effect, not characterizable. With separate discharges of the coil, it gave a fine but still faint restoration from extinction, which was strengthened by tension, but not affected by compression.

*Valeral*,  $C_5H_{10}O$ , is stronger than the last, and clearly positive. With moderate charges of the jar it gave a good but abrupt effect, strengthened by tension, but not affected by compression. With the coil, the effect was very strong, still not affected by compression ; but the contrast between tension and compression was regular and perfectly clear, proving the liquid to be purely positive, but a very weak insulator.

*Enanthol*,  $C_7H_{14}O$ , is still stronger, and purely positive. As a conductor, without the jar, it gave a clear though faint restoration. With moderate charges of the jar, the effect was good though still faint, strengthened by tension, and extinguished by compression. With strong discharges, the effect



was more intense but not so pure, the liquid being much disturbed.

*Benzoyl hydride*, or oil of bitter almonds ( $C_7H_5O, H$ ), is positive, and a very weak insulator. Without the jar, it gave a clear restoration, too abrupt for the hand-compensator. With moderate charges of the jar, the effect was still extremely quick but certainly positive, strengthened by tension, and not affected by compression.

*Ethylene monacetate*,  $C_4H_8O_3$ , ranks with the other acetates and the formates as very impurely positive. With weak discharges of the jar, the effect was too faint to be characterized, or even regularly seized; and with strong discharges of the coil, the liquid was very much disturbed. With moderate charges the effect was to all appearance positive, but very impure at the best.

*Methyl salicylate*, or oil of wintergreen,  $C_8H_8O_3$ , is purely positive. As a conductor, without the jar, it gave a sensible but very faint restoration. With strong charges of the jar, the effect was pretty strong and certainly positive, the contrast between tension and compression being clear and regular, though there was no weakening in any case by compression.

The effect was examined afterwards more closely with the Ruhmkorff-discharges, and with a special eye-piece described in one of my former papers—an acute prism of glass, revolving regularly round the line of vision, and exhibiting the progress of the phenomenon in time as an extension in space. Viewed in this way, the effect was strengthened by tension as formerly, and was also extinguished regularly and perfectly by compression. I have already referred to this form of experiment as one that would afford a clear proof of the *purity* of positive or negative character of a dielectric, in cases where the hand-compensator gives a sensible increase of intensity when *conspiring* with the electric strain, but no sensible decrease when *opposing* it.

23. *Beeswax* is purely negative, as are also all the fused fats that have been examined, with the exception of spermaceti, which is strongly positive.

*Palm-oil*, *cacao-butter*, *lard*, and *tallow* were tried successively in the fusion-cell as examples of the fats. There was generally a little disturbance by movements in the liquid; but the optical effects were distinctly and regularly negative, strengthened by compression, and neutralized by tension.

*Spermaceti* was then tried in the same way, and was found to be purely positive, like sperm-oil among the fixed oils; but it was much stronger than was expected, stronger indeed than any of the negative fats. As a nonconductor, and with a half

or quarter turn of the plate, it gave a strong and purely positive effect from extinction, without sensible disturbance of any kind.

A thing noticed in most of the fused fats, and strikingly apparent in the case of spermaceti, was the sluggishness of rise and fall of the electro-optic action. When strong electric force was applied, the optical effect rose gradually to its full intensity, through 1 or nearly 2 seconds; and again, when the apparatus was discharged, the light fell to sensible extinction still more slowly, through 20 or more seconds. This was evidently a thing of the same kind as the gradual rise and fall of effect which I observed long ago in glass; but the electric stress in that case was much more intense, and the duration of the phenomenon much greater, extending even to 20 or 30 minutes.

*Beeswax*, purified but unbleached, was tried in the same way as the fats, and was found to be purely negative, and almost as strong as spermaceti.

White wax, a colourless and very clear plate in the fusion-cell, gave a finer and stronger effect, still purely negative.

#### *Other Compounds of C, H, N.*

24. *Aniline*,  $C_6H_7N$ , is purely negative. Two samples were examined. One of them, tried with plate machine and strongest charges of the jar, gave a faint effect which was purely negative, strengthened by compression, and extinguished by tension. The other sample, which was much deeper in colour, gave no trace of effect with the jar; but with the Ruhmkorff's coil it gave intense restorations, which were purely negative by both tests.

*Allylamine*,  $C_3H_5NH_2$ , is very feebly negative. With the Ruhmkorff-discharges, the restorations from extinction were perfectly clear and regular, but very difficult to characterize. Upon the whole, the effect appeared to be certainly negative; but it was very faint, and somewhat impure at the best.

*Capronitrile*,  $C_6H_{11}N$ , is feebly but clearly negative. Was tried in the same way as allylamine, and acted rather better, the restorations from extinction being very pure and regular, but still rather difficult to characterize. On the whole, the effect was clearly negative, strengthened by compression, and not affected by tension.

*Benzonitrile*,  $C_6H_5CN$ , is purely and strongly positive. Tried as a conductor, without the jar, it gave an intense and very fine effect, which was strengthened by tension parallel to lines of force, and extinguished perfectly by compression.

This dielectric reminded me of nitrobenzol; but the action was much less abrupt, and therefore more easily characterized.

*Azobenzol*,  $C_{12}H_0N_{12}$ , fuses at  $65^{\circ}C$ . into a clean and transparent liquid of a deep red colour. Tried in the fusion-cell as a conductor, with increasing charges of the jar, it gave a series of fine and increasingly brilliant effects, all purely positive.

*Diphenylamine*,  $C_{12}H_{11}N$ , fuses at  $54^{\circ}C$ . into a transparent, colourless, and very volatile oil. Tried in the fusion-cell as a conductor, with moderate charges of the jar, it gave a pretty strong effect which was purely positive. With strong charges, the regular effect was masked in some degree by movements in the liquid.

*Dimethylaniline*,  $C_8H_{11}N$ , is purely positive. Tried in the plate cell as a conductor, without the jar, it gave a good restoration, which was too quick to be characterized. With small charges of the jar, the effect was very strong and purely positive, strengthened by tension, and extinguished by compression.

*Conine* gave no trace of effect, even with the strongest discharges of the coil. My sample was almost opaque, and certainly far from pure.

#### *Compounds containing Cl or Br.*

25. *Benzyl chloride*,  $C_7H_7Cl$ , is clearly positive, but acts only as a conductor. Tried with the jar, it gave no effect with 5 turns, a good effect with 10 or more turns; strengthened always by tension, and sensibly weakened by compression. My sample was not very clean.

*Chlorobenzol*,  $C_7H_6Cl_2$ , is purely positive. Acted well, though feebly, as a nonconductor, giving an effect which was strengthened by tension and extinguished by compression.

*Ethylene chloride*,  $C_2H_4Cl_2$ , is uncertain. It did give a faint and apparently regular effect with strong discharges; but the disturbance (as in the formic ethers) was excessive, and made the determination of the sign impossible. The results obtained with the next liquid make it probable, if not certain, that the failure in the present case was due to impurity of the sample.

*Ethylene bromide*,  $C_2H_4Br_2$ , is purely and strongly positive. Tried as a nonconductor (spark  $\frac{1}{8}$  inch), it gave a fine steady restoration, which was strengthened by tension, and extinguished perfectly by compression. As a conductor, with increasing charges of the jar, it gave a series of fine effects, which rose through a large range of intensity, always purely positive.

*Chloroform*,  $\text{CHCl}_3$ , is purely negative and pretty strong. As a nonconductor, it gave a fine and purely negative restoration from extinction. As a conductor, with increasing charges, it gave a set of increasingly brilliant effects, always purely negative, extinguished perfectly by tension parallel to lines of force. With strong discharges, there was a fine exhibition of extinction-bands, narrow and strong, brought in by tension parallel to lines of force.

*Bromoform*, as was expected, is also purely negative, but weaker than chloroform. As a conductor, with the jar, it gave a clear effect with 5 turns, strong with 10 or more turns, and always purely negative.

*Acetyl chloride*,  $\text{C}_2\text{H}_3\text{OCl}$ , is purely negative. As a conductor, with strong charges of the jar, it gave an effect from extinction which was merely strong enough to be characterized as certainly negative, being strengthened by compression, and weakened by tension. With the coil afterwards, there was a certain disturbance produced in the liquid by each discharge; but the regular effect was clearer and stronger than formerly, and always negative by both tests.

*Chloral*,  $\text{C}_2\text{Cl}_3\text{OH}$ , is positive. As a conductor, with the jar, it gave a good restoration with 10 or more turns of the plate. The effect was regularly strengthened by tension, but not sensibly affected by compression.

*Chloropicrin*,  $\text{CCl}_3\text{NO}_2$ , is purely negative. Tried as the last, it gave a clear effect with 5 turns, strong with 10 or more turns; and the restored light was always strengthened by compression, and always extinguished by the proper tension.

26. *Carbon tetrachloride* is purely positive, like the dichloride (formerly examined), but much weaker. Tested for insulation, it gave a good spark ( $\frac{1}{4}$  inch) from the prime conductor. The optical effect was not proportionably strong, not visible indeed from pure extinction; but with the assistance of the hand-compensator it was brought out very clearly, and was found to be purely positive. There was no advantage obtained by trial of the liquid as a conductor, with or without the jar.

*Sulphur chloride* is purely positive. As a conductor, with strong changes of the jar, it gave a faint but good effect, which was strengthened by tension, and clearly weakened by compression.

*Phosphorus trichloride* is purely negative, and stronger than the last. As a conductor, with small charges of the jar, it gave a moderately strong restoration from extinction; and the effect was regularly strengthened by compression, and extinguished by tension.

*Other Compounds and Solutions.*

27. *Amyl sulphocyanide*,  $C_6H_{11}NS$ , is positive. As a conductor, without the jar, it gave distinct restorations, too faint and quick to be characterized. With strong charges of the jar, the effect was strong, and always distinctly positive though very abrupt, strengthened by tension, and not affected by compression.

*Allyl sulphocyanide*, or oil of mustard-seed,  $C_3H_5CNS$ , is positive. With strong charges of the jar it gave a clear effect, which was too abrupt for the hand-compensator, but apparently positive. With the Ruhmkorff-discharges the effect was stronger and still very abrupt; but it was certainly positive, strengthened by tension, and not affected by compression. With very strong discharges the liquid was considerably disturbed.

*Thialdine*,  $C_6H_{13}NS_2$ , fuses into a transparent plate at  $43^\circ C$ . In the fusion-cell, with moderate charges of the jar, it gave a clear effect, pretty strong but very abrupt, certainly negative, being regularly strengthened by compression, and not affected by tension.

*Oil of sage* is purely positive. The initial extinction was imperfect, the liquid being a weak photogyre. With small charges of the jar, there was a good and purely positive restoration from extinction.

28. Several aqueous solutions were tried in the plate cell, but with no results worth mentioning, except in the two cases of  $Cl$  and  $SO_2$ .

*Chlorine* in water is feebly but purely negative. The water was distilled specially for the experiment, saturated with the gas, and then examined immediately. With strong discharges of the coil, there were distinct restorations from extinction, very faint but perfectly regular, clearly strengthened by compression, and clearly weakened by tension. The effects were to me barely visible; but they were as distinct as any very faint effects could be; they were also recovered regularly on repetition of the experiment, and with two successive charges of the liquid.

*Bromine* in water had been examined some time before, and had been entered in my note-book as very apparently, but very feebly, negative.

$SO_2$  in water is also purely negative. The experiment was made immediately after a similar one with water alone; and the contrast between the two was perfect, water being regularly and purely positive, and  $SO_2$  in water as regularly and purely negative, but rather feebler. The solution of sulphurous



acid was not noticeably stronger or weaker electro-optically than the chlorine solution.

*Summary.*

29. The principal results of the experiments are briefly summed up in the following statements, the numbers of the corresponding articles being attached in each case for reference.

The elementary bodies bromine, phosphorus, sulphur, all in the liquid state, are purely and strongly positive (3).

The hydrocarbons are nonconductors and purely positive, without known exception. The induction effected up to this time is a mere beginning in such an immense field; but it includes examples of the alcohol radicals or their hydrides, of the benzol series, of the olefines, the paraffins, and the terebenes; also cinnamol and naphthalin. Among the hydrocarbons, great density is generally accompanied by high electro-optic power (4).

The common alcohols are negative as a class. From the higher members downwards, the negative electro-optic power diminishes regularly, till it passes, in the last step of the series (ethyl to methyl), from feeble negative to feeble positive. Distilled water also is distinctly positive (5).

Of the series of fatty acids, those liquid at ordinary temperatures are in constant opposition of sign to the corresponding alcohols; they are also very much stronger. Of those that are solid at ordinary temperatures, two have been examined in a state of fusion, and are found, on the contrary, to be strongly negative (6, 7).

Of other alcohols and acids, the allyl, benzyl, cinnyl alcohols are negative; the diatomic glycol and the triatomic glycerin are feebly and impurely negative; phenol is distinctly positive, though in its chemical relations rather an alcohol than an acid; the oleic and lactic acids are both positive, the former strong, the latter very feeble (8).

The oxides of ethyl and amyl are purely negative, and stronger than the corresponding alcohols. Amyl oxide is a moderately good insulator, and one of the best negative dielectrics yet known (9).

The haloid ethers are purely positive, and rise in power from one series to another in the order I, Br, Cl; they generally rise also in power from lower members upwards. Some of them show an extraordinary increase of insulating and electro-optic powers as the experiment proceeds. Amyl chloride is one of the best positive dielectrics known; amyl bromide also is very strong (10, 11, 12).

The sulphides of the alcohol radicals are purely negative and weaker than the corresponding oxides, but much stronger than the alcohols. From lower members upwards they rise in electro-optic power (13).

The hydrosulphides are purely positive, and stronger than the corresponding fatty acids. From lower members upwards they rise in power (14).

Of the compound ethers, all that have been examined are clearly positive; and they include examples of the formates, acetates, butyrates, valerates, benzoates, nitrates, and nitrites. The optical effects are pure in the butyrates, but more or less disturbed in the others, impure in the acetates, very impure in the formates (15-21).

The following table contains a few additional bodies which are found to be electro-optically active. The optical effects are neither impure nor very weak, except in the cases that are so marked. The positive and the negative dielectrics appear always in the left-hand and right-hand columns respectively.

*Compounds of C, H, O (22, 23).*

Acetone (wk).	Aldehyde (wk).
Valeral.	Palm-oil.
Cenanthol.	Cacao butter.
Benzoyl hydride.	Lard.
Methyl salicylate	Tallow.
Ethene monacetate (imp.).	Beeswax.
Spermaceti.	

*Compounds of C, H, N (24).*

Benzonitrile.	Aniline.
Azobenzol.	Capronitrile (wk).
Diphenylamine.	Allylamine (wk).
Dimethylaniline.	

*Compounds containing Cl or Br (25, 26).*

Chlorobenzol.	Chloroform.
Benzyl chloride.	Bromoform.
Ethylene dibromide.	Chlorpicrin.
Chloral.	Acetyl chloride (wk).
Carbon tetrachloride.	Phosphorus trichloride.
Sulphur chloride.	

*Other Compounds and Solutions (27, 28).*

Amyl sulphocyanide.	Thialdine.
Allyl sulphocyanide (wk).	Cl in water (wk).
Oil of sage.	SO <sub>2</sub> in water (wk).

*Concluding Remarks.*

30. *Bodies under electric stress are birefringent, with reference to line of electric force as axis.*—This property has now been exemplified in such a number and such a variety of dielectrics, that it ought to be admitted as a general property of matter. There do occur cases (in the formic ethers &c.) in which the purity of electro-optic double refraction is lost : but these are no true exceptions to the general statement ; they are merely cases of disturbance, cases in which the regular effect is masked, wholly or partly, by the presence of other effects. Gross movements and heat appear to be the principal causes of disturbance.

*Dielectrics are divisible into two classes, the positive and the negative, corresponding to the two so-named classes of uniaxial crystals.*—This also has been abundantly confirmed by experiment, not as a rough adaptation of the notions and terms of Optics to our present subject, but as an exact physical truth. Except in cases of impure action or of mixed optical effects, cases which are comparatively rare in fact, the experimental contrast between the two kinds of dielectric is always as pure to sense, and under any tests yet applied, as is the contrast between quartz and Iceland spar. The two finest examples of the positive class are carbon disulphide and amyl chloride ; and these are far superior in power to any negative dielectric yet discovered. As interesting examples of the negative class, I select the following four, arranging them (according to my samples) in the order of descending powers :—amyl oxide, chloroform, capryl alcohol, aniline.

*Among bodies yet examined, the positive dielectrics are more numerous than the negative.*—Of 13 amyl compounds, 10 are purely positive, and 3 purely negative ; and similarly in other cases. Br, P, S, the only elements yet examined, are all purely positive.

*The electro-optic and chemical characters of compounds are closely connected.*—The hydrocarbons are positive, the fixed oils and fats negative, the fatty acids positive, the alcohols negative, &c.

*The electro-optic character of a chemical compound is not determined by its empirical formula.*—Isomeric bodies are sometimes electro-optically similar, and sometimes not. This is shown in the four following sets of isomers or polymers : propionic acid, methyl acetate, ethyl formate—all positive ; butyl alcohol and ethyl oxide, both negative ; aldehyde, butyric acid, ethyl acetate—the first negative and the other two positive ; allyl alcohol, acetone, caproic acid, methyl valerate—the first negative and the others positive.

Every chemically homologous series of bodies yet examined exhibits a certain constancy of electro-optic character.—Thus, the oxides, hydroxides, and sulphides of the alcohol radicals are negative; while the hydrosulphides, the iodides, bromides, chlorides, butyrates, benzoates, &c. are positive.

Through each of these homologous series, there is generally a progression of electro-optic power, the higher members being the stronger.—The common alcohols and the fatty acids (liquid at ordinary temperatures) afford very good illustrations. The two series of bodies are negative and positive respectively; and in each of the series, from member to higher member, there is a regular increase of absolute electro-optic power. The progression is not maintained in the higher parts of the acid series, the palmitic and stearic acids being (as the other fats are) strongly negative.

This progression, in singular cases, takes the form even of a change of sign.—The only examples yet known are afforded by the two last mentioned series, which begin thus:



This occurrence of contrary changes of sign at corresponding points of the two series is surely a very remarkable fact. The two following inferences are perhaps worthy of notice.

Oxygen is probably a negative dielectric.—Putting  $n=0$  in the general formulas of alcohol and acid, we obtain  $\text{H}_2\text{O}$  and  $\text{O}_2$  as the starting-points of the two series. Water and oxygen should therefore have the same signs as methyl alcohol and formic acid respectively. As far as water is concerned, the inference is confirmed already by experiment.

Our terms “positive” and “negative,” borrowed originally from *Physical Optics*, appear now to be terms intrinsically appropriate to the subject.—For in the acids we see a regular increase of positive power showing itself at one point of the series as a passage from  $-$  to  $+$ , and, again, in the alcohols a regular increase of negative power showing itself at one point as a passage from  $+$  to  $-$ .

31. *Electro-optic double refraction* is brought about by a special state of the dielectric, a state of essentially directional strain, which is a concomitant and a condition of the maintenance of electric stress. This appears to me to be a principle that must underlie any admissible explanation of the phenomena. The carefully grounded and very valuable conceptions of Faraday and Maxwell point in this one direction; and the simple facts of the case are, of themselves, quite decisive. What clearer manifestations of directional strain could be

desired than those that are presented here? There is, first, the *directional transmission of electric force* from limit to limit of the field; there is, secondly, the *special dioptric action of the force-transmitting medium*, an action precisely similar to that of glass *directionally strained by tensions or pressures*; and there is, finally, the *directional rupture of the dielectric* when the intensity of the transmitted force reaches a critical value characteristic of the medium.

I insist upon the essentially directional character of electric strain, in opposition to a theory of electro-optic action which has been advanced by Professor Quincke\*.

Electro-optic double refraction may be attributed to a quasi-crystalline and uniaxal structure, which is maintained by electric stress in the medium. I advanced this view of the phenomena in my first paper on the subject; and I still believe that it contains a germ of the truth. I think indeed that, to any one engaged with the facts of Electro-Optics, there is no theoretical conception that can present itself more naturally than that of an electrically induced structure, a regular arrangement of polarized molecules, roughly illustrated by the common "magnetic curves."

XXXII. *On the Electric Resistance of Carbon under Pressure.*  
By Professor SILVANUS P. THOMPSON, B.A., D.Sc.†

§ 1. **I**T has often been stated that the electric resistance of carbon decreases when subjected (1) to an increase of temperature, (2) to a mechanical compression. The first of these statements has been verified by so many authorities that there can hardly be any question of its correctness. The second I believe to be wholly misleading; for some careful experiments that I have lately made lead to the conclusion that the effect of mechanical compression upon the electric resistance of dense carbon is almost, if not quite, *nil*, and that what has been mistaken for an increase in electric conductivity is in reality merely better contact at the points of junction with the circuit.

§ 2. A preliminary experiment to test whether the alleged decrease of resistance by pressure was due to a true increase in specific conductivity or to better end-contact, was made in the following manner:—A thin cylindrical rod of Carré's dense artificial carbon (such as is used in electric lamps) was taken, its length being 72 centimetres. At a point about one

\* Phil. Mag. for July 1880, p. 37.

† Communicated by the Physical Society, having been read at the Meeting on February 25, 1882.



fourth of its length from the end a groove was filed round it, and around it was bound tightly the end of a clean thin copper wire. It was placed vertically upon a piece of copper in an upright frame, so that pressure could be applied longitudinally at the top; a flat piece of copper was placed upon the top of it and pressed lightly upon it. The point at which the thin wire was bound round it was then about 18 centim. from the lower end. The upper and lower portions were then connected up with a Wheatstone's bridge, provided, as in Kirchhoff's pattern, with a wire of German silver stretched over a divided scale, the resistances of the two parts of the wire right and left being (when balance was obtained in the galvanometer) proportional respectively to the resistances of the two portions of the carbon rod. The relative, not the absolute, resistances of the two portions were therefore being measured. Two bichromate cells supplied the requisite current, the galvanometer being a short-coil astatic instrument of simple form.

On trying the resistances, it appeared that the resistance of the longer part, which was uppermost, was somewhat greater in respect to that of the lower and shorter part than would have been expected from their relative lengths; the ratio of their resistances being 81 : 19, or about 4·25 : 1, whereas their lengths were as 3 : 1 almost exactly. After taking the rod out of its place and putting it back again under light contact at the top as before, the ratio was found to be 82 : 18, or 4·55 : 1. The rod was thus removed and replaced several times; and the ratio of the resistances was found to differ somewhat every time, the figures varying from 4·7 : 1 to 3·92 : 1. Pressure was now applied at the top of the rod, and the ratio of the resistances was again measured. With a load of 5 kilogrammes (as much as it was judged the rod would bear without risking breaking it), the ratio of the resistances was found to be much more constant and much nearer to the ratio of the lengths of the two portions, being 75·3 : 24·7, which is not very different from 3 : 1. It was therefore clear that the previous values had been greatly affected by the differences in contact at the two ends; the lower contact having less resistance than the upper, in consequence of the superincumbent weight of the rod and connexions—about 19 grammes in total.

§ 3. Another rod of Carré's carbon was next examined, and its actual resistance measured in ohms. Its length was 42·6 centim., its diameter 0·48 centim. To prepare it for the experiment, it was electroplated with a thin coating of copper to the length of about 1 centim. at each end, the extremities being afterwards scraped bare of copper so that end-contacts

should be made against the carbon itself. Copper wires were then carefully soldered to the copper coating at about 0.5 centim. from the ends. The object of this arrangement was to render possible a comparison between the resistance of the rod when there was merely end-contact—which might be more or less perfect according to the pressure—and the resistance of the rod as measured when there was a perfect contact through the deposited coatings of copper. The rod was then laid in a horizontal frame, where it reposed on two Y-shaped bearings—one end pressing against a lever-arrangement for the purpose of putting on a measurable amount of pressure, the rod being fixed at the other end by abutting against a brass set-screw. A copper piece was introduced between the lever and the extremity of the rod, in order to provide an end-contact; and arrangements were made whereby the rod could be connected up in a Wheatstone-bridge, the connexion being made at pleasure either through the end-contacts or through the copper-plated junctions.

The resistance of the rod between the copper-plated junctions was then measured, the rod being free at both ends. It was found to be  $0.56 \pm 0.007$  ohm. The end-contacts were then made to touch lightly (the circuit through them remaining open). The resistance through the copper-plated junctions showed no change. Pressure was then applied to the rod longitudinally, and augmented until it began to show lateral distortion, the effective force along the rod being 4150 grms., equivalent (if the area of cross section of the rod be taken as 0.18 square centim.) to 23,055 grms. per square centimetre. Yet, even under this pressure, not the smallest change could be detected in the resistance between the copper-plated junctions. If there was any, it was certainly less than 0.005 ohm, or less than 1 per cent. of the whole resistance.

The circuit was now made through the end-contacts by moving the set-screw until the lightest possible contact was obtained, the connexions through the copper-plated junctions having been thrown out of circuit. The resistance thus determined was 1.1 ohm. Pressure was applied as before. The resistance fell to 0.72 ohm when the pressure of 23 kilogrammes per square centimetre was reached. On releasing the pressure, the resistance again rose until contact became as light as possible. The resistance attained 1.08 ohm, when it rose abruptly to infinity as the set-screw ceased to touch the end of the rod. The battery and galvanometer used throughout were the same as described above.

Nothing could be more significant than these observations. When perfect contact was ensured by electroplating, pressure

produced no effect on the resistance of the carbon rod, or one inappreciably small. When circuit was made by pressing pieces of copper and brass against the rough ends of the carbon rod, contact was only imperfectly obtained, and the resistance varied with the pressure because increased pressure brought about better contact, or contact at a greater number of points.

The bearing of these observations upon the theory of the carbon rheostat, the carbon relay, the carbon transmitting-telephone, and the carbon microphone is obvious.

University College, Bristol,  
February 1882.

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XXXIII. *On the Determination of Chemical Affinity in terms of Electromotive Force.*—Part V. By C. R. ALDER WRIGHT, D.Sc. (Lond.), F.R.S., Lecturer on Chemistry and Physics in St. Mary's Hospital Medical School\*.

*On the Relationships between the Electromotive Force of a Daniell Cell and the Chemical Affinities involved in its Action.*

102. **I**N accordance with the theorem stated in § 61, the E.M.F. that would be requisite to break up a given electrolyte under given conditions into the "nascent" products of electrolysis would be a constant amount, were it not that the secondary physical and chemical actions of the electrodes, and of dissolved gases, &c. upon the nascent products give rise to the development of an amount of heat, the energy equivalent to which diminishes the work that would otherwise be done by the current whilst effecting electrolysis; so that the E.M.F. corresponding to the net electrolytic work actually done is less than the constant amount that would be requisite in the absence of these interfering circumstances; under certain conditions, the diminution in the work is so great that work is gained instead of spent, when the cell becomes an electromotor. Experiment shows that, *cæteris paribus*, the amount of diminution is less the more rapid the rate of current-flow; so that in a decomposing cell, in which, on the whole, work is spent during the passage of the current in doing electrolysis (the heating effect due, in accordance with Joule's law, to the resistance proper of the cell being left out of consideration), the counter E.M.F. set up (representing the work so spent) is of + sign, and increases in magnitude with the rate of current-flow; whilst in an electromotor, in which, on the whole, work is gained during the passage of the current, the counter E.M.F. set up is of - sign (*i. e.* is a

\* Communicated by the Physical Society, having been read at the Meeting held February 11, 1882.

direct E.M.F.), and decreases in magnitude with the rate of current-flow.

This decrease in magnitude, although a phenomenon well known under the name of "polarization of the cell," has nevertheless been less thoroughly investigated than is desirable. Thus, for instance, in the case of a given Daniell cell it is unknown to what relative extents the diminution is due to each of three entirely different possible causes, viz.:—first, the formation, in consequence of the electrolytic actions going on, of a stronger zinc-sulphate solution round the zinc plate, and of a weaker copper-sulphate solution round the copper plate, than were there originally; secondly, the more or less incomplete action as regards setting up E.M.F. of the energy gained by the solution of the zinc, and displacement thereby of copper from the copper-sulphate solution; and, thirdly, the somewhat analogous want of completeness in transformation into E.M.F. (and quantity of electricity jointly) of the energy gained by the transformation into ordinary copper of the nascent metal thus set free. In order to refer briefly to this possible want of completeness in development of E.M.F., it will be convenient to term that portion of the energy due to the various actions taking place in the cell that does contribute to the setting-up of difference of potential, the "adjuvant" portion of this energy; whilst the remainder is spoken of as the "non-adjuvant" energy. Of course the non-adjuvant energy in practice makes its appearance in the form of heat developed *ab initio*, and not in accordance with Joule's law—*i. e.* not due simply to the passage of a current through a resistance.

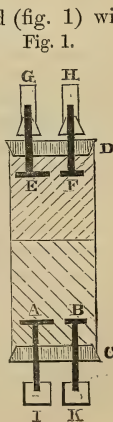
As regards the possible non-adjuvancy of energy thus indicated, it is to be noticed that whilst the observations of numerous experimenters agree in showing that, under certain conditions, at least an approximate equality subsists between the electromotive forces actually developed in a Daniell cell, and in various analogously constructed cells, and those corresponding to the net chemical changes taking place therein (*viz.*, in the case of a Daniell cell, the displacement of copper from copper sulphate by zinc), this approximate equality does not exist under all conditions even in a Daniell cell, inasmuch as, first, considerable discrepancies exist between the values obtained by different observers working under different conditions, and, secondly, the same cell exhibits values varying with the rate of current-flow through so-called "polarization;" whilst, on the other hand, with certain forms of cell the maximum E.M.F. developed falls considerably short of that corresponding to the net chemical action. These discrepancies and amounts of falling short appear to be in certain cases considerably greater than can be accounted for by the

formation of solutions of zinc and copper sulphates &c. of different densities through "migration of the ions," thus indicating considerable extents of non-adjuvancy.

In order to obtain further information upon these points, a large number of observations have been made upon various forms of Daniell cell and allied combinations; the general results of which are that, with the normal Daniell combination (zinc, zinc sulphate, or dilute sulphuric acid, copper sulphate, copper), the amount of non-adjuvant energy with suitable plate-surfaces and with feeble rates of current-flow is insensible, but becomes very considerable with more rapid rates of flow, or with certain impure forms of metallic plate-surfaces—the non-adjuvancy being partly due to incomplete development as E.M.F. of the energy due to the solution of the zinc, but more especially to the imperfect development as E.M.F. of that due to the transformation of nascent into ordinary copper; whilst the formation of solutions of densities different from those of the fluids originally employed also contributes to the diminution in the effective E.M.F. of the cell. With certain other forms of cell, more or less non-adjuvancy exists under all circumstances. In the following paper only those experiments referring to the normal Daniell cell are described, the remainder being postponed to a later occasion.

*Experiments made to determine the total fall in E.M.F. through so-called Polarization, occurring in variously arranged Daniell Cells for definite amounts of increase in the rates of Current-flow.*

103. A gravity Daniell cell was constructed (fig. 1) with two zinc plates, A and B, supported so that their upper surfaces were in the same horizontal plane, by means of stout wires passing through an indiarubber cork, C, the under surfaces of the plates, and the wires between the cork and plates, being covered with gutta percha. This cork fitted into the lower end of a wide glass tube some 4 or 5 centim. in diameter and 12 or 15 long; at the other end was a precisely similar cork arrangement, D, carrying two copper plates, E and F, of which only the lower surfaces were uncovered with gutta percha. The plates A and E were each of such size as to expose precisely 2.5 square centim. of surface, whilst the plates B and F each exposed double that area. In order to arrange the cell as a gravity battery, a concentrated zinc-sulphate solution (sp. gr. nearly 1.4) was run into the cell until half full, and





then a cold-saturated solution of copper sulphate (sp. gr. somewhat below 1.2) was carefully floated on the top of the zinc-sulphate solution. In some experiments this disposition of the plates was reversed, the copper plates being lowest and the zinc plates highest; in these cases saturated copper-sulphate solution was first poured in, and then a lighter zinc-sulphate solution. To avoid the almost inevitable contamination of the zinc-sulphate solution with faint traces of copper sulphate which occurs when the former is poured on to the latter, no matter how carefully done, it was found more satisfactory to fill the cell half full of the zinc-sulphate solution, and then slowly to introduce the copper sulphate at the base of the cell through a U-tube passing through the cork C, the end inside the cell being drawn out to a point and bent downwards, so that the copper-sulphate solution flowed in gradually and lifted up the zinc-sulphate solution without passing into it as a jet and so more or less impregnating it with copper.

It is evident that, since A and B, E and F are respectively in the same horizontal planes, the resistance of the column of fluid between the plates, R, must be sensibly the same, whether the smaller pair of plates, B and F, or the larger pair, A and E, be employed to generate a current; either of which can at pleasure be done by simply connecting the mercury-cups G H I K, attached to the appropriate plates, with the extremities of a known external resistance. By measuring the difference of potential E subsisting between the ends of this resistance the current passing, C, is known; hence if R be known, the E.M.F. of the cell,  $e$ , is known, being given by the equation

$$e = E + CR.$$

The value of R can be deduced, with a fair amount of precision, from the results of two series of observations with varying currents, made, first, with the smaller, and, secondly, with the larger pair of plates, in the following way:—By dividing the actual current-strengths by 2.5 and 5.0 (the superficies in square centimetres of the plates respectively), two series of values of E for corresponding “current-densities” (rates of flow per square centimetre of plate surface) are obtained, by interpolation from which, for a given current-density D, two values,  $E_1$  and  $E_2$ , are deduced for the smaller and the larger pair of plates respectively. The E.M.F. with the smaller pair,  $e_1$ , is manifestly

$$e_1 = E_1 + 2.5 DR,$$

whilst that with the larger pair is

$$e_2 = E_2 + 5.0 DR.$$

It is evident that, when the density of the current is the same, and the surfaces of the two copper and of the two zinc plates are respectively in the same conditions, the effect on the E.M.F. caused by the passage of a current must be sensibly the same, inasmuch as the same amount of zinc is dissolved and of sulphate of zinc formed, and the same quantity of copper is deposited and of copper sulphate decomposed, per square centimetre of plate surface ; so that  $e_1$  must sensibly  $= e_2$ .

Hence, since

$$E_1 + 2.5 CR = E_2 + 5.0 CR,$$

it results that

$$R = \frac{E_1 - E_2}{2.5 D}.$$

By contrasting in this way the values of the E's obtained with various current-densities, a set of values for R are obtained, fairly concordant when the observations are carefully made and the plates of such materials as to remain in the same condition of surface throughout the experiment, or nearly so, so that on introducing a given external resistance into the circuit, sensibly the same values for the E's are uniformly obtained. With sulphate-of-zinc solution surrounding the zinc plates, and with amalgamated plates (copper as well as zinc), this permanence is more readily ensured than when dilute sulphuric acid is used (with amalgamated zinc plates), or when the copper plate is not amalgamated, but only freshly coated with electro-deposited metal. Indeed, to obtain a sufficient number of readings when dilute sulphuric acid is employed, it is preferable to discharge the cell after an hour's use and recharge it, amalgamating the plates afresh, and filling up with the same solutions as before to exactly the same levels (ensured by suitably marking the glass), so that the resistance of the cell may vary as little as possible, the temperature being so adjusted as to be sensibly the same on the average throughout. Thus the following series of values was obtained as the average result of four sets of readings alternately with gradually increasing and gradually diminishing external resistances, with a cell containing nearly saturated copper-sulphate solution, freshly electro-coated copper plates, amalgamated zinc plates, and dilute sulphuric acid of 1.045 sp. gr., the plates being reamalgamated and reelectro-coated respectively for each successive series—all the observations being reduced to the same standard as that adopted throughout this paper, viz. the average reading at 15.5 of a large number of Clark's cells taken as 1.457 volt\*.

\* The exactness of this value depends not only on how far the average of these cells is identical with the average of those which served as the basis

Smaller plates.			Larger plates.		
C <sub>1</sub> .	D <sub>1</sub> .	E <sub>1</sub> .	C <sub>2</sub> .	D <sub>2</sub> .	E <sub>2</sub> .
·001738	·0006952	·869	·00385	·000770	·770
·000960	·0003840	·960	·001854	·0003708	·927
·000509	·0002036	1·018	·000999	·0001998	·999
·0002112	·00008448	1·056	·0005195	·0001039	1·039
·0001075	·00004300	1·075	·0002136	·00004262	1·068
·0000543	·00002172	1·085	·0001085	·00002170	1·085
·0000273	·00001092	1·092	·0000546	·00001092	1·092
·00001057	·00000423	1·097	·0000262	·00000524	1·097
·00000533	·00000213	1·100	·0000108	·00000216	1·100
·00000215	·00000086	1·103	·00000535	·00000107	1·103
·00000107	·00000043	1·103	·00000215	·00000043	1·103
·00000052	·00000021	1·103	·00000105	·00000021	1·103

104. From these figures the following values for R are deduced—the first four determinations only of each series being employed, on account of the smallness of the differences between E<sub>1</sub> and E<sub>2</sub> in the other cases:—

of Clark's valuation (Proc. Roy. Soc. xx. p. 444), but also on the exactness with which the B.A. unit of resistance is determined. If this latter be too small—as appears probable from the experiments of Joule, and of the writer and Mr. Rennie (Phil. Mag. March 1881, p. 169), from the results of Rowland, and from the recent experiments of Lord Rayleigh and Prof. Schuster—the true value of an average Clark's cell is below 1·457 to the same proportionate extent: thus, if the B.A. unit be really 0·99 earth-quadrant  
second, the E.M.F. of an average Clark's cell is only  $0·99 \times 1·457 \times 10^6 = 1·442 \times 10^6$  C.G.S. units. In view, however, of the fact that the question of the amount and even of the direction of the error (if any) in the B.A. resistance unit is not yet absolutely settled, it is assumed in this paper that there is no error at all.

For analogous reasons the value of J is assumed, as previously, to be  $42 \times 10^6$  ergs, the evidence in support of its having a higher value still being not inconsiderable; although the probability is that, if the B.A. resistance unit be only 0·99 earth-quadrant  
second, J is close to  $41·5 \times 10^6$ . The

value of  $\chi$  (the electrochemical constant defined in § 7) deduced in § 9 as the most probable, viz. ·000105, is also adhered to, notwithstanding that Mascart's recent experiments (*Comptes Rendus*, xciii. p. 50) tend to indicate that this value is too large, ·0001044 representing his final result: this value is 0·8 per cent. lower than ·00010527, the mean value deduced from Kohlrausch's experiments. If J be taken =  $41·5 \times 10^6$ , and  $\chi$  be assumed = ·0001048 (mean of Mascart and Kohlrausch's results), the value of  $\chi J$ , the factor for reducing gram degrees to C.G.S. E.M.F. units, becomes 4349, or 1·4 per cent. less than 4410, the value hitherto assumed, and still retained in this paper.

Prof. S. P. Thompson applies the term "Faraday coefficient" to the numerical value  $\chi$  (Journ. Soc. Arts, xxx. p. 34); should this term be generally accepted, the letter F might gracefully be used instead of  $\chi$  to indicate the factor, just as J is used to indicate the Joule coefficient.

D.	E <sub>1</sub> .		E <sub>2</sub> .		E <sub>1</sub> - E <sub>2</sub> .	R = $\frac{E_1 - E_2}{2.5 \times D}$ .
	Observed.	Interpo- lated.	Observed.	Interpo- lated.		
·000770	...	·847	·770	...	·077	4·00 ohms.
·0006953	·869	...	...	·799	·070	4·03 "
·0003840	·960	...	...	·921	·039	4·05 "
·0003708	...	·965	·927	...	·038	4·11 "
·0002036	1·018	...	...	·997	·021	4·12 "
·0001998	...	1·019	·999	...	·020	4·04 "
·0001039	...	1·050	1·039	...	·011	4·24 "
·0000845	1·056	...	...	1·047	·009	4·28 "
Average .....						4·11 ohms.

Taking 4·11 ohms as the average value of R, the following numbers are calculated from the above observations, the values of E<sub>1</sub> and E<sub>2</sub> being obtained by interpolation:—

Values from observations with smaller plates.				Values from observations with larger plates.			Average value of E.M.F. of cell.	Fall.
D.	E <sub>1</sub> .	2·5 × DR.	$e_1 = E_1 + 2.5DR.$	E <sub>2</sub> .	5·0 × DR.	$e_2 = E_2 + 5.0DR.$		
0	1·103	...	1·103	1·103	...	1·103	1·103	0
·000001	1·103	...	1·103	1·103	...	1·103	1·103	0
·000002	1·100	...	1·100	1·100	...	1·100	1·100	·003
·000005	1·096	...	1·096	1·097	·001	1·098	1·097	·006
·00001	1·092	·001	1·093	1·092	·002	1·094	1·094	·009
·00002	1·086	·002	1·088	1·086	·004	1·090	1·089	·014
·00005	1·072	·005	1·077	1·065	·010	1·075	1·076	·027
·0001	1·051	·010	1·061	1·041	·021	1·062	1·062	·041
·0002	1·019	·021	1·040	·999	·041	1·040	1·040	·063
·0004	·957	·041	·998	·916	·082	·998	·998	·105
·0007	·868	·072	·940	·798	·144	·942	·941	·162

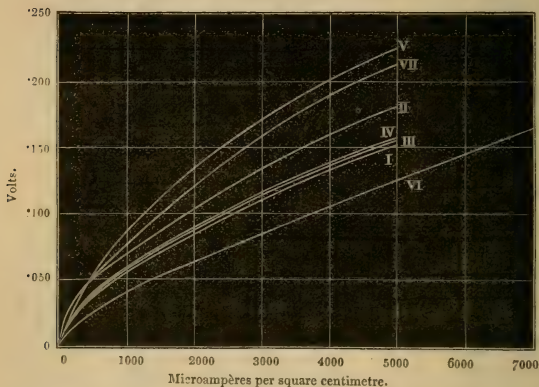
It is evident that the values of  $e_1$  and  $e_2$  accord so closely that their average may fairly be taken as representing, with but little error, the E.M.F. of a cell containing copper and zinc plates in the condition of those experimented with in this instance\*.

105. In various other analogous experiments the concordance was usually not quite so close as in this example, a smaller number of readings (one or two sets only) being made;

\* It might appear at first sight that a third valuation of the E.M.F. of the cell might be deduced as follows:—Since  $e_1 = E_1 + 2.5DR$ , and also  $e_2 = E_2 + 5.0DR$ , it results that  $e_1 = e_2 = 2E_1 - E_2$ ; but it is evident that this value is such that  $e_1$  is the arithmetical mean between  $e_2$  and  $2E_1 - E_2$ , and hence that the average of the three values must be identical with  $e_1$ , and therefore less exact than the mean of  $e_1$  and  $e_2$ .

but the discrepancy was in no case so great as materially to influence the general character of the curve representing the variation in the value of the E.M.F. with varying currents, obtained on plotting the results by making the currents abscissæ and the electromotive forces ordinates. The following table (p. 273) exhibits, side by side, the values obtained in various cases selected as specimens: in numerous other cases not quoted, the curves obtained were considerably similar to those indicated by the figures given in the table and represented in fig. 2. The

Fig. 2.



resistance of the cell,  $R$ , is stated in ohms, and the electromotive forces in volts; the "maximum E.M.F." indicates the average value of the highest E.M.F. observed throughout the various series of readings, this value being always observed when either no current at all circulated, or a current of less magnitude than about 8 microampères\* per square centimetre. The copper plates were uniformly surrounded by nearly saturated copper-sulphate solution (sp. gr. 1.175); the zinc plates were sometimes surrounded by nearly saturated zinc-sulphate solution (sp. gr. about 1.4), and were then lowest; in other cases they were highest, and were then surrounded either by zinc-sulphate solution of sp. gr. 1.10, or by dilute sulphuric acid of sp. gr. 1.045.

\* In accordance with the nomenclature adopted by the recent International Electrical Congress, the term *ampère* is used throughout this paper to indicate what in the former papers of this series was designated a *weber*, viz. 0.1 C.G.S. current-unit; so that a microampère = 0.000001 C.G.S. current-unit =  $10^{-7}$  ampère.



[illegible]

It is noticeable that whilst experiments Nos. I. and II. show that the curves obtained are by no means necessarily identical even when the conditions are sensibly the same (owing apparently to differences in the character of the copper deposited during the action of the cell), experiments Nos. I., III., and IV. indicate that but little difference in the curve is brought about by using commercial instead of pure zinc, or by altering the surface of the zinc by covering the bright metal with a film of copper (although more or less marked depressions in the maximum E.M.F. are occasioned thereby); on the other hand, experiments V. and VII., as compared with the others, indicate that amalgamating the copper renders the rate of fall in E.M.F. sensibly more rapid. But little difference, on the whole, is apparently occasioned in the curves by the use of zinc-sulphate solution (whether stronger or weaker than the copper-sulphate solution), as compared with dilute sulphuric acid; what difference is brought about is of this kind—that the sulphuric-acid curves slightly underlie the zinc-sulphate curves.

In none of the experiments made was any measurable depression of the E.M.F. of the cell brought about when the current flowed at a rate not exceeding 8 microampères per square centimetre; and in several cases this rate of flow might be doubled before any depression greater than 0.001 volt (0.1 per cent.) was occasioned. As a rule, when the current-density was from 30 to 50 microampères per square centimetre, a diminution in the E.M.F. of from 0.5 to 1 per cent. was brought about; whilst diminutions of 10 per cent. and upwards were occasioned when the current-density exceeded 3000. Supposing the same values to hold for ordinary Daniell cells (which is probably not quite the case, as the zinc and copper plates are usually unequal in size), it results that, with cells of ordinary dimensions (*e. g.* holding a litre and exposing a surface of 500 square centimetres), no appreciable diminution in the E.M.F. would be brought about when the current does not exceed  $500 \times 8 = 4000$  microampères (0.004 ampère); whilst diminutions of several tenths per cent. would be occasioned with currents of fivefold magnitude (0.02 ampère), and diminutions of 10 per cent. and upwards when the current exceeds  $500 \times 3000 = 1,500,000$  microampères (1.5 ampère).

*Experiments made to determine the maximum Electromotive Forces of variously arranged Daniell Cells containing Zinc-sulphate solution around the zinc, and the maximum proportion of the Fall in the E.M.F. of the Cell with gradually increasing currents, that could be due to accumulation round the plates of fluids of different densities through the migrations of the ions.*

106. A long series of experiments was next made with the object of determining how far the very considerable diminution in the E.M.F. of a Daniell cell, above shown to exist when moderately strong currents are generated, can be accounted for by the strengthening of the solution of zinc surrounding the plate, and the weakening of the copper-sulphate solution round the copper plate, which necessarily take place in consequence of the migration of the ions accompanying the passage of the current. Inasmuch as the use of dilute sulphuric acid introduces complications, these observations were made in the first instance with zinc-sulphate solutions only round the zinc plates; later on (§ 111), similar experiments with cells containing sulphuric acid are described.

It results from the experiments of Moser (*Annalen der Physik*, iii. p. 216) and H. F. Weber (*Phil. Mag.* [5] viii. pp. 487 & 523), that when a stronger solution of zinc (or copper) sulphate diffuses into a weaker one of the same salt, plates of zinc (or copper) placed in the two solutions acquire different potentials, that in the stronger solution being at the higher potential: the potential difference reckoned per a constant difference in specific gravity of solution (*e. g.* a difference of 0.1) is not constant, but depends on the actual values of the specific gravity, being less the stronger the solutions. The maximum value obtained (in the case of zinc-sulphate solutions containing respectively 60 and 1 per cent. of crystallized salt) was only .036 Daniell, or about .040 volt; whence it would seem that if the effect produced by zinc-sulphate solution in diffusing into copper-sulphate solution is of the same order of magnitude as that produced by diffusing into another zinc-sulphate solution of strength equivalent to that of the copper-sulphate solution, the effect on the E.M.F. of a Daniell cell, due to migration of the ions, cannot possibly materially exceed .04 volt; whilst, whatever the magnitude of the effect, it must tend to diminish the E.M.F. of the cell, since it partially equalizes the difference of potential between the zinc and copper plates set up by the chemical action alone. In order to find out the actual magnitude of the diminution due to this diffusive action in various cases, a number of determi-

nations were first made of the E.M.F. set up in various forms of Daniell cell when generating currents of magnitude not exceeding 8 microampères per square centimetre (and usually when generating no current at all), the zinc- and copper-sulphate solutions being in any given case of the same specific gravity\*. The average values being thus fixed, the observations were then repeated, using solutions not of the same specific gravity. It is particularly noteworthy in this connexion, that the E.M.F. of a Daniell cell was found to be *sensibly independent of the strength of the solutions when both are of the same specific gravity*—i. e. the deviations observed from equality were less than the experimental errors.

The cells employed were constructed of two small beakers—one containing zinc-sulphate solution and plates of zinc (scraped bright, covered with electro-deposited metal, or amalgamated with pure mercury), and the other copper-sulphate solution and similar copper plates. The two beakers were connected, in the way described by Raoult (*Ann. de Chim. et de Phys.* 4th series, ii. p. 317, and iv. p. 392), by means of an inverted Y-tube, the ends of which, dipping into the two beakers respectively, were covered over with thin bladder, the tube being filled with the zinc-sulphate solution. Each one of the zinc and copper plates used was soldered to a platinum

\* Although two solutions of zinc and copper sulphate, respectively of the same specific gravity, are not absolutely chemically equivalent to one another (i. e. do not contain precisely equivalent percentages of the two salts), yet the difference in specific gravity between any two solutions of equivalent strengths is so small that, for all practical purposes, it may be assumed that when the specific gravity is the same the solutions are of equivalent strengths. Direct determinations of the specific gravities of various solutions of equivalent strengths (made by dissolving known weights of the air-dry pure salts to known weights of aqueous solutions), gave the following results:—

Percentage of $\text{CuSO}_4, 5\text{H}_2\text{O}$ .	Specific gravity at $18^\circ$ .	Equivalent percentage of $\text{ZnSO}_4, 7\text{H}_2\text{O}$ .	Specific gravity at $18^\circ$ .
1	1.006	1.15	1.007
3.75	1.023	4.3	1.026
7.5	1.047	8.6	1.053
15	1.098	17.2	1.107
22.5	1.156	25.9	1.163
30	1.214	34.5	1.223

The 30-per-cent. solution of copper sulphate was slightly supersaturated, and deposited crystals on standing in a closed vessel; saturated zinc-sulphate solution has a specific gravity upwards of 1.4. It is noteworthy that these figures indicate that when given bulks of water and of either zinc- or copper-sulphate solution are mixed, an *increase* in bulk occurs, thus agreeing with J. Thomsen's result that dilution of a solution of either salt is accompanied by heat-absorption (§ 113).

wire fused into a piece of glass tubing, forming a mercury-cup; the soldering and the whole length of the platinum wire being thickly covered with gutta percha, so that only zinc (or copper) was exposed to the fluid. The plates were then connected with a series of mercury-cups in such a way that, by simply moving a double switch connected at one end with two mercury-cups in connexion with the electrometer-quadrants, and dipping at the other end into two of the series of cups, any required pair of zinc and copper plates could be brought into connexion with the electrometer. Fig. 3 shows the arrangement used for two pairs of plates, and fig. 4 that for

Fig. 3.

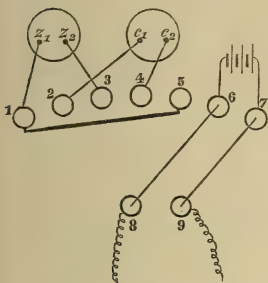
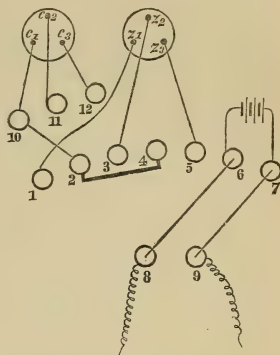


Fig. 4.



three pairs. In the former the two zinc plates,  $z_1$  and  $z_2$ , are connected with mercury-cups Nos. 1 and 3 (No. 1 being also connected with No. 5), whilst the two copper plates,  $c_1$  and  $c_2$ , are connected with cups Nos. 2 and 4 respectively. Cups Nos. 6 and 7 are connected with a standard cell (the error of which, in reference to the average taken as 1.457 volt, is known). By means of a double switch any pair of the series of cups 1 to 7 can be connected with cups 8 and 9, which are connected with the electrometer through the usual reversing-gear; so that when Nos. 1 and 2, 2 and 3, 3 and 4, and 4 and 5 are thus connected, the electromotive forces due to the combinations  $z_1c_1$ ,  $c_1z_2$ ,  $z_2c_2$ ,  $c_2z_1$  are respectively read off; whilst when 6 and 7 are connected (as represented in the figure) the electrometer-scale is standardized. In actually taking readings a double set was always employed, the switch being successively used to connect the four combinations and the standard with the electrometer, and then to connect them



again in reversed order; so that, by taking the averages of the two sets, any error due to running down of the electrometer during the readings might be eliminated (in practice the running down during the period was insensible, the variation being usually at most only 2 or 3 per cent. during the whole day, and often much less). When three pairs of plates were used, the three zincs were connected respectively with cups 1, 3, and 5; whilst cup No. 2 was connected with No. 4, and also, by means of a movable wire, with either of three other cups, Nos. 10, 11, and 12, with which respectively the three copper plates were connected: so that when No. 2 was connected with 10, as represented in the figure, the combinations  $e_1z_1$ ,  $e_1z_2$ , and  $e_1z_3$  could be read off by connecting the double switch with 1 and 2, 2 and 3 (or 3 and 4), and 4 and 5 successively; and similarly for the other combinations.

107. The ultimate results of upwards of a hundred series of valuations of the electromotive forces of various combinations, mostly lasting over four hours, were as follows:—

(1) With the stronger solutions used (specific gravities 1·100 to 1·175) the E.M.F. set up after the first few minutes remained sensibly constant for several hours (the temperature being constant), never differing from the final average of the four average sets of readings made in each of the first four hours by amounts outside the limits of observational error. For instance, the following values were obtained in one experiment, in which the temperature throughout was close to 18°, the specific gravity of the solutions being 1·175:—

Combination.	Average E. M. F. determined during the				Final average.
	1st hour.	2nd hour.	3rd hour.	4th hour.	
Amalgamated zinc— electro-copper ...	1·112	1·113	1·114	1·114	1·1132
Bright zinc—electro- copper .....	1·110	1·109	1·112	1·110	1·1102
Amalgamated zinc— bright copper ...	1·119	1·122	1·122	1·120	1·1207
Bright zinc—bright copper .....	1·117	1·115	1·118	1·118	1·1170

Very similar results were obtained in all the other cases. After twenty-four hours the E.M.F. usually diminished to a greater or less extent. These changes are referred to later on (§ 108), being probably due to oxidation of the metals by dissolved air.

(2) With weaker solutions (sp. gr. 1·0065 to 1·050) the E.M.F. developed during the first half hour or so was usually

slightly lower than the value attained subsequently; which value remained sensibly constant for several hours, and then fell to a greater or lesser extent, as with the stronger solutions. Accordingly, in such cases the lower readings during the first half hour or so were not taken into account in the final average. For any given combination of plates, the final average thus obtained with weaker solutions was sensibly identical with that obtained with the stronger solutions\*.

(3) The combinations that gave the most constant results on repetition of the experiments were those containing amalgamated zinc and either electro-copper or amalgamated copper; next to which were those with electro-deposited zinc and these same kinds of copper plates. Combinations containing either bright zinc or bright copper (*i. e.* rods of fused metal or sheets of rolled metal filed, scraped, or sand-papered to perfect brightness) exhibited a considerably wider range of variation. By comparing various bright copper plates with one and the same amalgamated zinc plate, or various bright zinc plates with one and the same electro-copper plate, it was found that differences, amounting nearly to 0.010 volt in the

\* The conclusion that the E.M.F. developed by a given pair of plates immersed, the one in zinc-sulphate, the other in copper-sulphate solution, is sensibly independent of the strength of the solutions when both are of the same density (or, at least, that the variation in E.M.F. caused by variation in strength of the solutions is not outside the limits of experimental error), is further corroborated by the results of still more direct experiments on the matter. Three cells were arranged, containing solutions respectively of the specific gravities 1.010, 1.090, and 1.175, each containing a recently electro-coppered plate and a freshly amalgamated zinc plate. A number of readings were taken of the potential-differences subsisting between the plates in each case; and then the plates were exchanged—the pair from the first cell being placed in the second, that originally in the second being transferred to the third, and so on. After a new set of readings had been taken, the plates were again exchanged and a third set of readings taken; so that each pair of plates was read in each cell. The following figures were finally obtained, all readings taken during the first half hours after immersion of the plates being rejected:—

Specific gravity 1.010.	Specific gravity 1.090.	Specific gravity 1.175.
1st pair of plates 1.1127	2nd pair of plates 1.1122	3rd pair of plates 1.1125
2nd " " 1.1130	3rd " " 1.1115	1st " " 1.1118
3rd " " 1.1140	1st " " 1.1135	2nd " " 1.1133
Mean ..... 1.1132	Mean ..... 1.1124	Mean ..... 1.1125

In each case the value found as the mean for the three pairs of plates differs from the general average 1.1127 by an amount so small as hardly, if at all, to be outside the limits of experimental error.

most extreme instances, were observable in each case with different bright plates as compared with one another. On the other hand, on comparing various electro-copper or amalgamated copper plates with one and the same zinc plate, or various amalgamated zinc plates with one and the same copper plate, the extreme ranges of fluctuation were found to be not more than half those observed with bright plates, and usually did not exceed  $\pm \cdot 001$  as compared with the average.

(4) As the ultimate average result of all the determinations made, it was found that an amalgamated zinc plate gave, when opposed to a given copper plate, an E.M.F. lower by  $\cdot 002$  volt than a bright zinc plate, and lower by  $\cdot 001$  volt than an electro-zinc plate. The actual differences in various experiments ranged in the former case between  $+\cdot 006$  and  $-\cdot 004$ , the bright zinc plate sometimes giving a higher value, and sometimes a lower value, than the amalgamated plate—more frequently the former. (In the example quoted above, the bright zinc plate gave a value lower by  $\cdot 0030$  when opposed to an electro-copper plate, and by  $\cdot 0037$  when opposed to a bright copper plate.) With electro-zinc as compared with amalgamated zinc, the difference ranged between  $+\cdot 004$  and  $-\cdot 003$ , the electro-zinc sometimes giving a higher and sometimes a lower value than the amalgamated zinc, more usually the former.

(5) Similarly, the effect of substituting a bright copper plate for an electro one in any given combination was uniformly to cause an increase in the E.M.F. by an amount varying between  $\cdot 001$  and  $\cdot 010$  volt, and averaging, on the whole,  $\cdot 006$ . (In the example quoted above, bright copper gives a higher value than electro-copper by  $\cdot 0075$  when opposed to amalgamated zinc, and by  $\cdot 0068$  when opposed to bright zinc.) The effect of amalgamating a copper plate was found to be, on the whole, to give an E.M.F. lower by  $\cdot 001$  than that given under the same conditions by a freshly electro-coppered plate, the actual difference ranging between  $+\cdot 002$  and  $-\cdot 003$ , the amalgamated plate sometimes giving a higher value and sometimes a lower one than the electro-plate, more frequently the latter. It is worthy of notice that no sensible difference was observable whether the plate amalgamated were previously of bright rolled metal or of electro-metal; so that, on the whole, the effect of amalgamating a bright rolled plate was to depress the E.M.F. by  $\cdot 006 + \cdot 001 = \cdot 007$ .

(6) The average results of all the experiments made are contained in the following tabular statement: increase in E.M.F. is indicated by the + sign, and diminution by the — sign:—

Variation in the E.M.F. due to the use of zinc- and copper-sulphate solutions of different strengths between the limits of sp. gr. 1·0065 and 1·175, both solutions being of the same specific gravity in any given case . . . } Less than  $\pm \cdot 001$ .

	Maxi- mum.	Mini- mum.	Range.	Ave- rage.
Effect of substituting for fresh electro-copper :—				
Bright rolled copper sheet .....	+·010	+·001	·009	+·006
Amalgamated copper (surface wet with fluid mercury) .....	+·002	—·003	·005	—·001
Effect of substituting for fresh electro-zinc :—				
Bright cast zinc .....	+·005	—·005	·010	+·001
Amalgamated zinc (surface wet with fluid mercury).....	+·003	—·004	·007	—·001
Electromotive force of combinations :—				
Amalgamated zinc—Amalgamated copper ...	1·115	1·110	·005	1·113
"    "    Electro-copper .....	1·116	1·111	·005	1·114
"    "    Bright copper .....	1·124	1·115	·009	1·120
Electro-zinc—Amalgamated copper .....	1·116	1·110	·006	1·114
"    "    Electro-copper .....	1·118	1·111	·007	1·115
"    "    Bright copper .....	1·124	1·114	·010	1·121
Bright zinc—Amalgamated copper .....	1·119	1·109	·010	1·115
"    "    Electro-copper .....	1·121	1·110	·011	1·116
"    "    Bright copper.....	1·126	1·112	·014	1·122

108. The above figures are, as already stated, derived from the observations made during the first four hours after setting up the cells, the values registered during the first half hour or so with weaker solutions being rejected on account of their frequently being lower than the sensibly constant values attained to subsequently. When the cells were allowed to stand for twenty-four hours, or for longer periods, a greater or less fall in the E.M.F. was usually noticed: by taking out any pair of the plates (*e. g.* the amalgamated zinc and the electro-copper plates) and replacing them by a freshly prepared similar pair, it was found that the value rose again to sensibly the same value as on the previous day when only set up a few hours; so that by taking out first one and then the other of the pair of plates, determinations could be made of the amount of the total fall attributable to alterations of either plate separately. The actual values thus obtained fluctuated considerably. As a general rule, it was found that bright copper plates gave the same value after twenty-four hours' immersion as they did at first; but occasionally the value was lowered by ·002 to ·004. Electro-copper plates usually gave values less by ·002 or ·003

after twenty-four hours than at first; and in some instances, when the pink electro-metal was sensibly browned or discoloured by oxidation, either all over or here and there in spots, the diminution was even greater, sometimes as much as  $\cdot 010$ . Amalgamated copper plates, if the surface were still white and brilliant after twenty-four hours, gave the same value as at first; but if the mercury had sunk into the copper, and brown spots of oxidized metal were here and there visible, the E.M.F. was a few thousandths of a volt lower than at first. With the zinc plates greater diminutions were, as a rule, observed. In some cases amalgamated plates showed little or no diminution after twenty-four hours; but generally a diminution of  $\cdot 002$  to  $\cdot 005$  was observed; whilst with bright and electro-zinc plates diminutions of from  $\cdot 001$  to  $\cdot 015$  were noticed. On the whole, after twenty-four hours the E.M.F. was sometimes unchanged, and sometimes less by  $\cdot 020$ . After forty-eight hours the fall was more perceptible still, the few combinations that had not appreciably altered during twenty-four hours always showing a decided fall after a longer period. It is noticeable in this connexion, that cells after Daniell's construction, but containing other metals than copper, did not always give the same results as normal Daniell cells. Thus, for instance, whilst cells containing cadmium sulphate and cadmium plates behaved like copper Daniells, in that the E.M.F. was sensibly steady for some hours after first setting up, and only exhibited a measurable fall after several hours had elapsed, and not always then, analogous cells containing silver sulphate and silver plates invariably showed a perceptible fall in less than an hour after first setting up, the diminution becoming progressively greater as a longer time elapsed. That this diminution was due to a change (presumably oxidation by dissolved air) induced on the surface of the zinc plate was rendered evident by the fact that, on taking out from such a zinc-silver cell the zinc plate after the lapse of an hour or more, and opposing it to electro-copper in an ordinary zinc-copper Daniell, an E.M.F. was indicated considerably less than the value given by a fresh zinc plate, and usually just about as much less as represented the fall in E.M.F. observed with the zinc-silver cell at the end of the period during which it was observed, as compared with the E.M.F. at the beginning of that period, when it was newly set up.

109. It is further to be noticed, that all the above-mentioned figures were obtained with cells the nature of the construction of which was such that diffusion of copper-sulphate into the zinc-sulphate solution, and consequent deposition of copper on the surface of the zinc, *did not take place at all* during the whole time that the observations lasted. With ordinary



gravity-cells it is almost impracticable to prevent traces of copper reaching the zinc after some twenty-four hours at latest: the effect of the deposition of even the faintest traces of copper on the zinc surface is to cause a considerable fraction of the energy due to the solution of the zinc to become non-adjuvant, and thus materially to diminish the E.M.F. Thus, for instance, the following figures were obtained with one cell, and similar ones in numerous other cases:—

E.M.F. of gravity-cell newly set up: zinc plate	} 1·103
wholly free from copper . . . . .	
After 8 hours: faint tarnish visible on the zinc .	1·095
„ 24 hours: slight film of copper on the zinc .	1·070
„ 48 hours: thick film of copper on the zinc .	1·045

In much the same way, the presence of even small quantities of impurities in the zinc causes an appreciable diminution in the E.M.F. In all the above-described observations, some of the purest zinc that could be bought was employed, being fashioned into plates and rods by melting in a porcelain crucible, pouring out on a fire-clay tile, and cutting into slips with a chisel, &c. When commercial sheet or cast zinc was used, or when pure zinc was amalgamated with imperfectly purified mercury, the E.M.F. developed when such zinc was opposed to a given copper plate was often very materially less than the value obtained with pure zinc, or pure zinc and pure mercury. Thus, whilst values varying between 1·111 and 1·116 were obtained with pure amalgamated zinc opposed to fresh electro-copper as above described, values varying from 1·080 to 1·109 were obtained with commercial zinc amalgamated with pure mercury, and with pure zinc amalgamated with impure mercury, similarly opposed.

It is abundantly evident from the above-described results (not to speak of those detailed later on), that “the E.M.F. of a Daniell cell” is a unit of comparison subject to decidedly wide limits of fluctuation; but that it is possible to reproduce a standard cell of the kind within a maximum limit of variation of about  $\pm 0\cdot25$  per. cent., by using Raoult’s form of construction together with a recently electro-coppered or amalgamated copper plate, and a pure zinc plate amalgamated with pure mercury, the zinc- and copper-sulphate solutions used being both of the same specific gravity, the precise value of the specific gravity being immaterial. Even when made, however, such a standard cell cannot be relied on for more than a few hours. It will be shown in a subsequent paper that whilst Latimer Clark’s mercurous-sulphate cell is subject to an even wider range of fluctuation in E.M.F. than the best forms of Daniell cell, its permanence

is very far superior, a well-constructed cell giving absolutely the same value (when used in conjunction with a quadrant electrometer only) for months and months together.

110. The above described experiments having given results indicating the average values of the electromotive forces developed with different characters of plates when the specific gravities of the solutions surrounding the plates are the same, further series of observations were made with cells in which the zinc- and copper-sulphate solutions were not of the same specific gravity, the mode of operating being otherwise the same as before. As predicable from Moser's figures, and as previously observed by H. F. Weber, it was found that when the copper-sulphate solution was the more dense of the two, the E.M.F. was higher than with solutions of equal density, and *vice versa* when the zinc-sulphate solution was the stronger. The average results of various observations, mostly lasting over four hours as before, are contained in the following table; in every case the zinc plate employed was of pure metal and amalgamated with pure mercury.

Effect of increasing the strength of the Zinc-sulphate solution relatively to that of the Copper-sulphate.

Specific gravity of solutions used.		Nature of copper plate.	Average E.M.F. at 18° of combination.			Ratio of difference in E.M.F. to difference in specific gravity.
Zinc sulphate.	Copper sulphate.		Observed.	Previously found for solutions of equal specific gravity.	Difference.	
1.145	1.010	{ Electro. Bright.	1.099	1.114	.015	$\frac{.014}{.135} = .105$
			1.107	1.120	.013	
					.014	
1.175	1.050	{ Electro. Bright.	1.102	1.114	.012	$\frac{.012}{.125} = .096$
			1.108	1.120	.012	
					.012	
1.260	1.050	{ Electro. Bright.	1.096	1.114	.018	$\frac{.0175}{.021} = .083$
			1.103	1.120	.017	
					.0175	
*1.395	1.010	{ Electro. Bright.	1.077	1.114	.037	$\frac{.0355}{.0385} = .092$
			1.086	1.120	.034	
					.0355	
*1.395	*1.175	{ Electro. Bright.	1.097	1.114	.017	$\frac{.0165}{.22} = .075$
			1.104	1.120	.016	
					.0165	

Effect of increasing the strength of the Copper-sulphate solution relatively to that of the Zinc-sulphate.

1·010	1·090	{ Electro. Bright.	1·129 1·135	1·114 1·120	·015 ·015	$\frac{·015}{·080} = 0·188$
					·015	
1·010	*1·175	{ Electro. Bright.	1·132 1·141	1·114 1·120	·018 ·021	$\frac{·0195}{·165} = ·118$
					·0195	
1·050	*1·175	{ Electro. Bright.	1·126 1·133	1·114 1·120	·012 ·013	$\frac{·0125}{·125} = ·100$
					·0125	
1·090	*1·175	{ Electro. Bright.	1·123 1·128	1·114 1·120	·009 ·008	$\frac{·0085}{·0085} = ·100$
					·0085	

It is evident from these figures that the accumulation round the zinc plate of zinc sulphate, and the exhaustion of the copper sulphate in the solution round the copper plate, even if carried out to the utmost possible extent, could not diminish the E.M.F. of a Daniell cell by more than ·03 to ·04 volt; whilst it is hardly probable, even with tolerably rapid currents, that the accumulation would suffice to diminish the E.M.F. by more than half that amount—a diminution almost negligible in comparison with the much larger amounts, 0·1 volt and upwards, found above to be due to this cause of diminution and non-adjuvancy jointly.

It is noticeable in passing that the above figures show that when two solutions of zinc and copper sulphates interdiffuse, the E.M.F. set up (like that produced by the interdiffusion of two zinc-sulphate, or of two copper-sulphate solutions, as studied by Moser) is of such a character that the stronger solution acquires the higher potential; the actual value of the E.M.F. developed also is *less for a given difference in specific gravity the stronger the solutions*, and, so far as the two sets of results can be compared, agrees fairly with the values deducible from Moser's experiments—indicating that the difference between the E.M.F. set up when two different solutions of { zinc  
sulphate diffuse into a constant copper } sulphate solution is  
zinc } substantially the same as the E.M.F. set up when these two  
different zinc } sulphate solutions diffuse into each other.  
copper }

\* Solution almost saturated at ordinary temperatures.

Moreover the effect of a given alteration in the strength of the zinc-sulphate solution (every thing else remaining the same) is sensibly equal in amount, but opposite in sign, to that of a similar alteration in the strength of the copper-sulphate solution; it is evident that only when this is the case can the E.M.F. of the cell be the same whether the solutions be strong or weak. It will be shown in a future paper that this property, though not absolutely peculiar to the normal Daniell cell, is still rather the exception than the rule with analogous voltaic combinations.

*Experiments with Daniell Cells containing dilute Sulphuric Acid.*

111. In all the above described experiments, the solution surrounding the zinc plate was one of pure zinc sulphate. Various previous experimenters, notably H. F. Weber, have found higher values for the electromotive forces of Daniell cells containing dilute sulphuric acid than for those containing zinc-sulphate solution (*vide* § 113): *à priori* a higher value might be anticipated, because a notable amount of heat is evolved on further diluting even weak sulphuric acid; so that the total energy gained in the cell is not merely that due to the displacement of copper from copper sulphate by zinc, but also that gained in the dilution of the sulphuric acid through the diffusion which necessarily goes on. On trying experiments of the same kind as those just described with cells containing dilute sulphuric acid of various strengths (the zinc being amalgamated), it was found that not only was there a considerable want of permanence in the E.M.F. set up, the values perceptibly decreasing after a period of time (varying in different cases from half an hour to several hours) had elapsed since setting up the cells, but, further, that two cells, apparently set up in identically the same way, exhibited much greater differences in their readings during the period before the E.M.F. began to diminish, than were observed in the zinc-sulphate cells examined as above described. On the whole, however, the average values obtained distinctly pointed to the conclusion that, when the acid and copper-sulphate solutions are of the same specific gravity, the E.M.F. rises with strength of the solution; and that when they are not of the same specific gravity (the acid not being stronger than specific gravity 1.18), the E.M.F. is sensibly that due to a cell containing liquids both of specific gravity equal to that of the acid in the cell examined, corrected by the addition (or subtraction) of a quantity representing the difference in specific gravity of the solutions multiplied by the numerical value

deduced from the zinc-sulphate cell experiments, representing the difference in E.M.F. produced by a variation in the specific gravity of the copper-sulphate solutions equal to that between the acid and copper sulphate in the cell examined: *i. e.*, if, for example, the E.M.F. of a cell containing both liquids of sp. gr. 1·100 be  $E$ , that of a copper-cell containing acid of sp. gr. 1·100 and copper-sulphate solution of sp. gr. 1·010 will be  $E - (1·100 - 1·010) \times \alpha$ , where  $\alpha$  is the factor expressing the diminution per unit difference of specific gravity in the E.M.F. between the limits of sp. gr. 1·010 and 1·100 for copper-sulphate solution. Similarly, that of a cell containing acid of sp. gr. 1·100 and copper-sulphate solution of sp. gr. 1·175 would be  $E + (1·175 - 1·100)\beta$ , where  $\beta$  is the corresponding factor for a difference in specific gravity between the limits 1·100 and 1·175.

Thus, for instance, the following values were obtained with a cell containing fluids both of sp. gr. 1·175, the temperature being close to 18° throughout.

Period since setting up.	During 1st hour.	2nd hour.	3rd hour.	4th hour.	Average.
Electro-copper plate .....	1·161	1·162	1·163	1·160	1·1615
Bright „ „ .....	1·167	1·168	1·168	1·166	1·1672

In most cases, however, a distinct fall of upwards of ·005 volt occurred in less than four hours.

A number of similar series of observations (upwards of thirty) with various other cells, in which the fluids were always of equal specific gravity, gave the following results, the observations being only continued as long as the E.M.F. remained sensibly constant—*i. e.* for a period of time varying from thirty minutes to four hours, and averaging about two hours. In all these experiments electro-copper and amalgamated pure zinc plates were employed.

Specific gravity of fluids.	Electromotive force set up, in volts.		
	Maximum.	Minimum.	Average.
1·010	1·143	1·121	1·129
1·050	1·150	1·128	1·139
1·090	1·155	1·137	1·148
1·175	1·179	1·161	1·169

Evidently, even with the weakest acid, the E.M.F. is sensibly above that developed with zinc-sulphate cells—*viz.* 1·114;



whilst with stronger solutions the difference is yet more marked.

112. A number of analogous observations were made with cells containing dilute sulphuric-acid and copper-sulphate solutions, not both of the same specific gravity: the average results were as follows:—

Specific gravity of solutions.		Excess of specific gravity of copper sulphate over acid solution.	Approximate correction for excess of specific gravity of copper sulphate.	Average E.M.F. observed.	Observed E.M.F. corrected for excess of specific gravity of copper sulphate.
Acid.	Copper sulphate.				
1·010	1·050	+·040	—0·008	1·147	1·139
1·010	1·090	+·080	—0·015	1·135	1·120
1·010	1·175	+·165	—0·019	1·137	1·118
				Average..... = 1·126	
1·050	1·175	+·125	—0·012	1·148	1·136
1·175	1·050	—·125	+0·012	1·168	1·180
1·175	1·090	—·085	+0·008	1·164	1·170
				Average..... = 1·175	

The final averages representing the E.M.F. corrected to the uniform specific gravities 1·010, 1·050, and 1·175 respectively, do not differ from the values directly obtained as just described for these specific gravities by amounts outside the limits of experimental error in this class of the various experiments made.

A peculiar result was obtained with cells containing sulphuric acid of sp. gr. 1·265, and nearly saturated copper-sulphate solution of sp. gr. 1·175. The E.M.F. was considerably depreciated, the average value in four sets of experiments with electro-copper and amalgamated pure zinc plates being only 1·084 (maximum 1·095, minimum 1·067). On standing a few hours, copper-sulphate crystals formed at the junction of the two fluids, showing a much less degree of solubility of the salt in the acid fluid formed than in pure water.

*Relationships between the maximum E.M.F. developed by a Daniell Cell and the Energy due to the net Chemical action taking place therein.*

113. The above-described results afford a ready explanation of the discrepancies between the valuations of the E.M.F. of a Daniell cell that have been made in absolute measure by various observers, amongst the more important of which may be cited those of Bosscha (*Pogg. Ann.* ci. p. 517, 1856), von Waltenhofen (*Pogg. Ann.* cxxxiii. p. 478, 1868),

Kohlrausch (Pogg. *Ann.* cxli. p. 456, and *Ergänz.* vi. p. 35), H. F. Weber (Phil. Mag. 1878, [5] v. p. 189), and J. Thomsen (Wied. *Ann.* xi. p. 246, 1880), all of which valuations lie between 1·088 and 1·132 volt when reduced to that unit (and, in the case of Bösscha's results, corrected for an error of about 8 per cent. in the value of the coil used by him). To these may be further added the electrostatic valuations of Sir W. Thomson and Latimer Clark, both of which lie near to 1·11 volt. Favre (*Comptes Rendus*, lxix. p. 35) and Raoult (*Ann. Chem. Phys.* [4] ii. p. 338, and iv. p. 392) obtained by methods involving calorimetric measurements numbers representing the "galvanic heat" of a Daniell cell, and equivalent to considerably smaller electromotive forces, their valuations (23993 and 23900 gramme-degrees respectively) corresponding to 1·058 and 1·054 volt. In these instances, and in the case of the lower values obtained by other observers, doubtless the "polarizations" produced by the passage of the tolerably powerful currents employed were considerable. The highest values were obtained with cells in which dilute sulphuric acid was used; thus, H. F. Weber found that a perceptibly higher value was obtained with such a cell than with one containing zinc-sulphate solution, viz. 1·1317 and 1·1286 (mean = 1·1301), as compared with 1·0954. That this should be the case is predicable from the nature of the heat-evolutions taking place when zinc is dissolved in acid of various strengths. Let an amount of heat,  $H_1$ , be evolved when a gramme-equivalent of zinc oxide is dissolved in sulphuric acid of given strength,  $\text{SO}_4\text{H}_2, m \text{ H}_2\text{O}$ ; and let  $H_2$  be the heat evolved on its solution in acid of a different strength  $\text{SO}_4\text{H}_2, n \text{ H}_2\text{O}$ ,  $n$  being less than  $m$ . Let the solution  $\text{SO}_4\text{Zn}, n \text{ H}_2\text{O}$ , resulting in this latter case, evolve  $h_1$  of heat on the addition of  $(m-n) \text{ H}_2\text{O}$ , so as to form the solution  $\text{SO}_4\text{Zn}, m \text{ H}_2\text{O}$ ; and let the heat evolved on the addition of this quantity of water to  $\text{SO}_4\text{H}_2, n \text{ H}_2\text{O}$ , so as to convert it into  $\text{SO}_4\text{H}_2, m \text{ H}_2\text{O}$ , be  $h_2$ . Then, if the zinc oxide were dissolved in the stronger acid, and the zinc sulphate diluted, the heat-evolution would be  $H_2 + h_1$ ; whilst if the acid were diluted first, and the zinc oxide were then dissolved in it, the total heat evolved would be  $H_1 + h_2$ . Since of necessity the two amounts of heat,  $H_2 + h_1$  and  $H_1 + h_2$ , must be equal, it results that  $H_2 = H_1 - h_1 + h_2$ . Now  $h_2$  is a considerable positive quantity in all cases; whilst Thomsen's results on the heat evolved on solution of salts in water (*Deut. chem. Ges. Berichte*, 1873, p. 710) indicate that when the solution is accompanied by heat-absorption (as is the case with zinc sulphate), a further heat-absorption takes place on diluting a stronger solution of the salt with water, so that  $h_1$  has a negative value. Hence, on both

accounts,  $H_2$  is greater than  $H_1$ ; that is, the work gained in the synthesis  $ZnO, SO_3 \text{ } x \text{ aq.}$  increases as  $x$  diminishes. Since the net chemical action in a Daniell cell is equivalent to the result of the actions  $(Zn, O) + (ZnO, SO_3 \text{ } x \text{ aq.}) - (Cu, O, SO_3 \text{ } y \text{ aq.})$ , it finally results that the chemical action taking place in the cell develops an amount of energy which increases, *ceteris paribus*, as  $x$  diminishes, *i. e.* is greater the more concentrated the acid surrounding the zinc.

On the other hand, when the zinc plate is surrounded by zinc-sulphate solution instead of sulphuric acid, the effect of variation in the strengths of the copper- and zinc-sulphate solutions will be comparatively but small when both are of the same degree of molecular concentration (which, as shown above, is very nearly the case when they are of the same density). If  $SO_4 Zn, nH_2O$  evolves, as before,  $h_1$  on addition of  $(m-n)H_2O$ , and  $SO_4 Cu, nH_2O$  evolves  $h_3$  on a similar addition, and if  $H_3$  and  $H_4$  are respectively the heats evolved when zinc displaces copper from  $Cu SO_4, nH_2O$ , and  $Cu SO_4, mH_2O$ , it results that, if zinc displace copper from the stronger solution and the resulting  $SO_4 Zn, nH_2O$  be diluted to  $Zn SO_4, mH_2O$ , the heat evolved will be  $H_3 + h_1$ ; whilst if the copper-sulphate solution be first diluted and then the zinc displaces the copper, the heat-evolution is  $H_4 + h_3$ . Since, of necessity,  $H_3 + h_1 = H_4 + h_3$ , it follows that  $H_3 = H_4 + h_3 - h_1$ . Now, since the solution of zinc and copper sulphates (crystallized) is in each case accompanied by heat-absorption, it results that  $h_3$  and  $h_1$  are both negative, and hence that  $h_3 - h_1$  is negligible if  $h_3$  is any thing like comparable with  $h_1$  in magnitude; so that in this case the energy developed by the net chemical action taking place in a Daniell cell must be practically independent of the degree of concentration of the solutions.

114. The earlier calculations of J. Thomsen, referred to in §16, as to the heat evolved in the displacement of copper from copper sulphate by zinc, are for various reasons probably less accurate than the later results obtained by him (*Journ. prak. Chem.* [2] xi. p. 412, and xii. p. 271); these different values may be thus contrasted, the values being grammes-degrees per gramme-molecule:—

Values from experiments by Andrews, Dulong, Hess, Favre and Silbermann, and J. Thomsen.	Values from later experiments of J. Thomsen.
$Zn, O, SO_3 \text{ aq.} = 108460$	106090
$Cu, O, SO_3 \text{ aq.} = 56216$	55960
Difference = 52244	50130
Corresponding in volts (per gramme-equivalent) to 1.152 } .....	1.105

The earlier value is deduced from observations in which the heat of formation of copper oxide from the metal by combustion is involved, the copper being in a more or less compact state, filings &c.; the latter involves the determination of the heat-evolution during the precipitation of *spongy* copper from copper sulphate by iron. Leaving out of sight other sources of difference between the two values, this affords a reason why the former value should be the higher, since heat is evolved in the transformation of spongy into compact copper\*. On the whole, it is evident that the net chemical change taking place in a Daniell cell (*i. e.* the displacement of copper from copper sulphate by zinc) corresponds to an E.M.F. which is a little higher than 1.105 volt by an amount which is the greater the more compact the copper precipitated, and is approximately constant when the zinc plate is surrounded by zinc-sulphate solution of the same equivalent strength as the copper-sulphate solution surrounding the copper plate, but is influenced by the strength of the dilute sulphuric acid when the fluid surrounds the zinc plate. The amount of this influence can be approximately calculated from Thomsen's determinations of the heat developed in the formation of the solutions of strengths indicated by  $\text{H}_2\text{SO}_4$ ,  $n\text{H}_2\text{O}$  where  $n$  varies (*Deut. chem. Ges. Berichte*, iii. p. 496). Thomsen finds in gramme-degrees per gramme molecule:—

$n$	gramme-degrees.	$n$	gramme-degrees.
9	14940	199	17056
19	16248	399	17304
49	16676	799	17632
99	16850	1599	17848

From which table the values for any intermediate values of  $n$  can be obtained by interpolation. In the experiments

\* That this is so is shown by the circumstance that if a current be sent through a decomposing-cell containing copper-sulphate solution and copper electrodes, of which the positive one is of compact rolled metal, a considerably higher difference of potential is set up, under any given conditions and with a steady current, than is set up when the + electrode is replaced by one covered with freshly electro-deposited metal. The more spongy texture of the latter corresponds to a greater heat-development during solution than that taking place with the compact metal, and hence to a diminution of the work that has to be done by the current in passing; with not very powerful currents the difference often exceeds .02 or .03 volt, corresponding to 450 to 700 gramme-degrees per gramme equivalent. In a somewhat similar way, but using the mercurial calorimeter, Favre found (*Comptes Rendus*, lxxiii. p. 1258) that electro-copper gave out about 1000 gramme-degrees more heat than rolled metal per gramme equivalent; this would correspond to an E.M.F. of .044 volt.

leading to the valuation 50130 gramme-degrees for the heat developed during the precipitation of a gramme molecule of copper by zinc, Thomsen used fluids containing altogether 800 molecules of water to one of zinc sulphate, &c. Hence, were the acid used in the synthesis  $\text{Zn, O, SO}_3 \text{ aq.}$ , to be  $\text{H}_2\text{SO}_4, 17 \text{ H}_2\text{O}$  (corresponding nearly to the sp. gr. 1.175), instead of  $\text{H}_2\text{SO}_4, 800 \text{ H}_2\text{O}$ , the heat-development would be greater than 106090 by  $17632 - 15986 = 1646$  gramme-degrees per gramme molecule (15986 being the heat of dilution of sulphuric acid when  $n=17$ , deduced from the above table): this corresponds to 823 gramme-degrees per gramme equivalent  $= .036$  volt; *i. e.* the E.M.F. corresponding to the heat-development during the displacement of copper from copper sulphate by zinc would be greater than 1.105 volt by .036, or would be 1.141 volt. To this amount should also be added the value of the E.M.F. equivalent to the heat-absorption during the dilution of  $\text{Zn SO}_4, 17 \text{ H}_2\text{O}$  to  $\text{Zn SO}_4, 800 \text{ H}_2\text{O}$ . In a similar fashion it is calculable that to the value 1.105 should be added the amounts .023, .019, and .008 volt when sulphuric acid of sp. gr. 1.090, 1.050, and 1.010 respectively surrounds the zinc, giving the sums 1.128, 1.124, and 1.113 respectively. Hence, finally, the following tables of values result:—

## Zinc surrounded by Zinc-sulphate solution.

Electromotive force corresponding to net chemical action.

Electromotive force observed.

$1.105 + x,$ where $x$ is a small quantity varying with the physical condition of the copper deposited.	Bright zinc opposed to bright copper . . . . .	1.122
	Bright zinc opposed to electro-copper . . . . .	1.116
	Bright zinc opposed to amalgamated copper . . . . .	1.115
	Amalgamated zinc opposed to bright copper . . . . .	1.120
	Amalgamated zinc opposed to electro-copper . . . . .	1.114
	Amalgamated zinc opposed to amalgamated copper . . . . .	1.113
	Electro-zinc opposed to bright copper . . . . .	1.121
	Electro-zinc opposed to electro-copper . . . . .	1.115
	Electro-zinc opposed to amalgamated copper . . . . .	1.114



## Zinc surrounded by dilute Sulphuric Acid.

Strength of acid.	Calculated electromotive force.	E.M.F. observed with electro-copper opposed to amalga- mated zinc.
$\text{H}_2\text{SO}_4$ , 358 $\text{H}_2\text{O}$ =sp. gr. 1.010	$1.113 + x + y$	1.129
$\text{H}_2\text{SO}_4$ , 67 $\text{H}_2\text{O}$ = „ 1.050	$1.124 + x + y$	1.139
$\text{H}_2\text{SO}_4$ , 37 $\text{H}_2\text{O}$ = „ 1.090	$1.128 + x + y$	1.148
$\text{H}_2\text{SO}_4$ , 17 $\text{H}_2\text{O}$ = „ 1.175	$1.141 + x + y$	1.169

where  $y$  is a small quantity corresponding to the heat absorbed on dilution of the zinc sulphate to  $\text{ZnSO}_4$ , 800 $\text{H}_2\text{O}$ .

It is hence evident that in all cases the agreement between the E.M.F. actually developed and that due to the net chemical and physical actions taking place is so close, that what differences exist lie within the limits of experimental error; so that, finally, the conclusion may be drawn that, under favourable conditions, the E.M.F. of a Daniell cell is that due to the net resultant of the various physical and chemical actions taking place, the whole of the energy being adjuvant, viz. that gained by the displacement from copper-sulphate solution of copper by zinc, together with that gained by the transformation into ordinary electro-metal of the "nascent" copper first thrown down by the action; whilst under other conditions the E.M.F. falls below this amount, even after making allowance for the effect of the migration of the ions in causing solutions of different specific gravities to accumulate round the plates, indicating non-adjuvancy of one or other or both of these component portions of the total energy gained.

*Experiments made with a view to find whether the Fall in E.M.F. on increasing the Current-density is mainly dependent on changes taking place in connexion with the actions at the surface of the Zinc or at that of the Copper plate.*

115. In order to trace out somewhat more completely, if possible, how far that amount of fall in the E.M.F. of a Daniell cell taking place as the current generated increases, which is not due to the accumulation of solutions of zinc and copper of different densities round the plates, can be attributed to actions taking place at one or the other plate respectively, the experiments described above (§103, 104) were repeated, with the difference that, instead of two sets of readings only being made (viz. when the two larger and the two smaller plates respectively were opposed), four sets were made—(1) when the two larger plates were opposed, (2) with the larger zinc and smaller copper, (3) with the two smaller plates, and

(4) with the smaller zinc and larger copper plates opposed. By interpolation from the direct observational results, the differences of potential between the plates for any constant current-value were then calculated in each of the four cases. By comparing the values thus obtained in cases (1) and (2) and in (4) and (3), two sets of differences were obtained, indicating the effects produced by halving the area of the copper plate, every thing else being the same throughout, saving that with results (1) and (2) the larger zinc plate, and with the other pair of results the smaller zinc plate, was opposed to the two copper plates respectively: although this modified the actual values obtained in each of the original sets of readings, yet it produced practically no effect on the differences. In just the same way, by comparing the interpolation values in cases (1) and (4) and in (2) and (3), two corresponding sets of differences were obtained, indicating the effects produced by halving the area of the zinc plate; as before, the two sets substantially coincided. Various experiments of this kind were made with different plate-materials and fluids surrounding them: whilst the numerical values obtained were found to be to some extent variable with these conditions, yet, on the whole, it was always found that *the effect of halving the area of the copper plate notably exceeded that of halving the area of the zinc plate*. For instance, the following numbers were obtained in one set of observations with a cell containing bright pure zinc plates surrounded by zinc-sulphate solution of sp. gr. 1.42, and freshly-coated electro-copper plates surrounded by copper-sulphate solutions of sp. gr. 1.175, the larger plates exposing a surface of 5.0 square centimetres, and the smaller ones exposing 2.5 square centimetres.

Effect of halving the area of the copper plate.							
Current, in micro- ampères.	Larger zinc plate opposed.			Smaller zinc plate opposed.			Mean differ- ence.
	(1) Larger copper.	(2) Smaller copper.	Differ- ence.	(4) Larger copper.	(3) Smaller copper.	Differ- ence.	
100	1.082	1.078	.004	1.076	1.073	.003	.0035
200	1.071	1.066	.005	1.064	1.060	.004	.0045
500	1.061	1.055	.006	1.052	1.047	.005	.0055
1,000	1.045	1.036	.009	1.035	1.026	.009	.0090
2,000	1.026	1.015	.011	1.011	.999	.012	.0115
5,000	.964	.947	.017	.950	.929	.021	.0190
10,000	.876	.843	.033	.854	.820	.034	.0335
20,000	.729	.672	.057	.698	.639	.059	.0580

Effect of halving the area of the zinc plate.							
Current, in micro- ampères.	Larger copper plate opposed.			Smaller copper plate opposed.			Mean differ- ence.
	(1) Larger zinc.	(4) Smaller zinc.	Differ- ence.	(2) Larger zinc.	(3) Smaller zinc.	Differ- ence.	
100	1·082	1·076	·006	1·078	1·073	·005	·0055
200	1·071	1·064	·007	1·066	1·060	·006	·0065
500	1·061	1·052	·009	1·055	1·047	·008	·0085
1,000	1·045	1·035	·010	1·036	1·026	·010	·0100
2,000	1·026	1·011	·013	1·015	·999	·016	·0145
5,000	·964	·950	·014	·947	·929	·018	·0160
10,000	·876	·854	·022	·843	·820	·023	·0225
20,000	·729	·698	·031	·672	·639	·033	·0320

116. In precisely the same way, the following mean difference-values were obtained in two other analogous experiments, in the first of which the zinc plates were amalgamated and immersed in zinc-sulphate solution sp. gr. 1·42, the copper plates being also amalgamated and immersed in copper-sulphate solution sp. gr. 1·175; and in the second of which electro-copper plates and copper-sulphate solution sp. gr. 1·175 were employed, conjoined with amalgamated zinc plates immersed in dilute sulphuric acid sp. gr. 1·045. The above mean difference-values are also exhibited in the table.

Current, in micro- ampères.	Amalgamated zinc and amalgamated copper—zinc sul- phate solution.		Amalgamated zinc and electro-copper —dilute sulphuric acid.		Bright zinc and electro-copper— zinc-sulphate solution.	
	Effect of halving area of		Effect of halving area of		Effect of halving area of	
	Copper.	Zinc.	Copper.	Zinc.	Copper.	Zinc.
100	·001	·001	·001	·001	·0035	·0055
200	·004	·002	·002	·003	·0045	·0065
500	·009	·003	·003	·005	·0055	·0085
1,000	·015	·004	·005	·007	·0090	·0100
2,000	·024	·005	·011	·010	·0115	·0145
5,000	·040	·009	·020	·015	·0190	·0160
10,000	·049	·017	·041	·020	·0335	·0225
20,000	·058	·026	·056	·032	·0580	·0320

Much the same kind of result was obtained in various other similar experiments; the effect of halving the area of the copper plate was, especially with the stronger currents, much more marked than that of halving the area of the zinc

plate. The actual value of the depreciation produced with the stronger currents in either case, moreover, clearly indicates that the diminution cannot possibly be solely due to the formation of stronger zinc-sulphate solution round the zinc plate, and weaker copper-sulphate round the copper plate, in the case of the smaller areas, than are produced with the larger ones; and hence the conclusion is arrived at that when, by reason of the production of a current, the E.M.F. of a Daniell cell is diminished, and the energy developed becomes proportionately non-adjuvant, the non-adjuvancy is ascribable, not merely to actions taking place at the surface of the zinc plate, but also, and more particularly, to those taking place at the surface of the copper plate. In the former case, the energy gained during the conversion of the metallic zinc of the plate into solution of zinc sulphate makes its appearance under such conditions partly as heat from the very commencement of the action, and is never wholly manifested as electric action expressible in volt-coulombs. In the latter case, the effect of the chemical action of the cell is to set free copper, which, in its transformation from the condition in which it is first set free (nascent copper) to the condition ultimately assumed (more or less compact electro-deposited soft coherent metal), causes a gain of energy which, like that due to the solution of the zinc, is partly manifested as heat *ab origine*, and is never, under such conditions, obtained wholly as electric action. The actual proportion of the energy due to the solution of the zinc or to the agglomeration (or allotropic modification) of the copper which is thus non-adjuvant, is variable within certain limits with the conditions of the experiment, the nature of the plate-surfaces and of the liquids in the cell, &c., but, *ceteris paribus*, is greater the stronger the current: with very feeble currents (of density not exceeding some 8 microampères per square centimetre), the proportion of non-adjuvant energy is too small to be measurable.

### *Summary of Results.*

117. The above-described experiments, and the conclusions to be drawn from them, may be thus summarized:—

1. When a Daniell cell is constructed with equal-sized plates of pure zinc and pure copper (either compact bright metals, amalgamated plates, or plates covered with electro-deposited metal) immersed respectively in solutions of pure zinc and copper sulphates of the same specific gravity, and is made to generate a current not exceeding in density some 8 microampères per square centimetre, an E.M.F. is set

up varying within certain small limits according to the precise condition of the surfaces of the metals as regards polish, oxidation, &c., but always lying fairly close to 1.115 volt, and practically identical with the E.M.F. corresponding to the energy gained in the net chemical change ensuing, viz. the displacement of copper from copper-sulphate solution by zinc; so that under these conditions practically all the energy gained is adjuvant, whether due to displacement of copper by zinc, or to transformation into ordinary metal of the "nascent" copper thus set free.

2. When impure zinc, or pure zinc amalgamated with impure mercury, is used, a greater or less amount of the energy gained is non-adjuvant, even under conditions such as would with pure zinc cause all the energy to be adjuvant. The source of this non-adjuvancy evidently lies in the nature of the actions taking place at the surface of the zinc plate; the maximum E.M.F. that such a cell can generate is more or less considerably below 1.115 volt, in some instances by several per cent.

3. When the density of the current exceeds 8 micro-ampères per square centimetre, the E.M.F. of the cell falls more or less below 1.115 volt, owing to three causes, each of which produces an effect in the direction of diminishing the E.M.F. First, according as the current density is greater or smaller, a greater or lesser degree of non-adjuvancy of the energy gained in the conversion of metallic zinc into zinc-sulphate solution is brought about. Secondly, a greater or lesser degree of non-adjuvancy is similarly brought about in the energy gained by the transformation into ordinary copper of the "nascent" metal liberated at the surface of the copper plate; other things being equal, this source of non-adjuvancy distinctly predominates over the other source just mentioned. Thirdly, the passage of the current causes a weaker solution of copper sulphate to be formed round the copper plate, and a stronger one of zinc sulphate to be produced round the zinc plate, than were originally used; this sets up an inverse E.M.F., and diminishes the effective E.M.F. of the cell. The maximum possible diminution due to this cause does not exceed .04 volt; whilst with a current the density of which amounts to .003 ampère per square centimetre and upwards, the total diminution due to this cause together with the non-adjuvancy amounts to several times this maximum possible value. The diminution due to these various causes jointly constitutes what is sometimes spoken of as the "polarization" of the cell.

4. When the solutions of zinc and copper sulphate em-



ployed are not of the same specific gravity, the E.M.F. of the combination differs from that which would have been set up had both been of the same specific gravity by an amount which increases with the difference in specific gravity of the two solutions: if the copper-sulphate solution is the stronger, the E.M.F. is increased, and *vice versâ*. The amounts of increase and decrease are sensibly the same as the electromotive forces generated when two copper-sulphate or two zinc-sulphate solutions interdiffuse, the specific gravities of which are identical respectively with those of the two fluids actually present in the cell examined. So long as the two solutions are of the same specific gravity, the E.M.F. set up is, *cæteris paribus*, sensibly independent of the actual value of this specific gravity; at least the fluctuations observed are not outside the range of experimental errors.

5. When dilute sulphuric acid is used instead of zinc-sulphate solution, its specific gravity being the same as that of the copper-sulphate solution, an increase in the E.M.F. of the cell is produced which sensibly corresponds with the increase in the "heat of formation" of zinc sulphate when sulphuric acid is employed of the strength used in the cell, as compared with acid diluted to a larger extent ( $\text{H}_2\text{SO}_4$ , 800  $\text{H}_2\text{O}$ ). If the copper-sulphate solution differs from the acid in specific gravity, the latter not exceeding 1.18 in specific gravity, the E.M.F. is raised above or lowered below what it would have been had the copper sulphate been of the same specific gravity, by an amount which is sensibly the same as the E.M.F. generated by the interdiffusion of two copper-sulphate solutions the specific gravities of which are identical respectively with those of the two fluids actually present in the cell examined.

6. Owing to the diminution in the E.M.F. of a Daniell cell when generating a current, the fluctuations in the maximum values obtainable with any given cell with the physical condition of the surfaces of the plates and the time that has elapsed since its construction, the tendency to deposition of copper on the zinc by diffusion and the consequent diminution in E.M.F., and the variation in E.M.F. according as dilute acid of different strengths or zinc-sulphate solution is used to surround the zinc plate, it results that "the E.M.F. of a Daniell cell" is a very variable standard of E.M.F. and one singularly devoid of permanence. By taking suitable precautions in the construction of a cell (using pure zinc amalgamated with pure mercury, amalgamated or electro-copper, and pure zinc- and copper-sulphate solutions of the same specific gravity), a cell may be obtained the E.M.F. of

which does not differ more than  $\pm 0.25$  per cent. from 1.113 or 1.114 volt, according as amalgamated or electro-copper is used; but such a cell cannot be kept many hours without altering in value materially, and is in practice a very far less convenient standard than the mercurous-sulphate cell of Latimer Clark; for, notwithstanding that the limits of variation between two cells of this latter kind, similarly prepared, are somewhat greater than those of the best form of standard Daniell cell, it nevertheless possesses the valuable property of remaining sensibly constant (the temperature being the same) for many months, and even one or more years, as will be more completely shown in a future paper.

#### XXXIV. Notices respecting New Books.

*Roorkee Hydraulic Experiments.* By Captain ALLAN CUNNINGHAM, R.E. Vol. I., Text pp. 399 + xvi. Vol. II., Tables—(1) Detailed Tables, (2) Abstract Tables, pp. 156 + xii; pp. 49. Vol. III., Plates, lii. Roorkee: Thomason College Press, 1880, 1881.

THESE volumes give an account of experiments, on Flow of Water in a Canal, which lasted about four years (December 1874 to March 1879, with some intermissions). We can hardly be expected to go through this mass of calculation, but will endeavour to put our readers *en rapport* with the results arrived at by Captain Cunningham in his valuable labours, as here carefully digested and served up for all whom they may concern. The mode of performing each experiment is given in great detail, not by any means a fault in investigations of this nature. In condensation, however, to the weakness of that bugbear, the general reader, a brief preface, or *résumé* of contents is attached to each chapter, giving “the gist of the chapter without experimental or argumentative detail.” Whatever data or results appear to the author to be doubtful are indicated by a query (?) attached. River-experiments on a small scale are well known not to be applicable to large bodies of water. India, with its many large canals, affords favourable opportunities for such experiments, as our author observes, “with a fair expectation of a practically useful result.”

The objects contemplated by Captain Cunningham were shortly these:—(1) discovery of a good method of discharge-measurement; (2) testing the applicability of known mean-velocity formulæ; (3) discovery of a good approximation to mean velocity: all three for large canals. The main results which are stated to have been arrived at are:—Loaded tube-rods give a rapid and sufficiently close approximation to mean velocity past a vertical; with good arrangements discharge-measurements obtained by the method advocated under similar conditions may be expected not to differ more than 3 per cent.; none of the known mean-velocity formulæ appear to be of really general applicability; central mean velocity-measurement

appears to be the best means of *rapid approximation* to mean (sectional) velocity, but the reduction must (at present) be effected by a coefficient to be *found by previous special experiment* at each site. Besides these the author enumerates several minor results of interest. Enough has been said to show that the work is a highly technical one; but though it is *caviare* to the general, it appears to be a most carefully compiled account of a series of experiments of great interest in its special department; and every thing has been done, in the way of tables, plates, and description, to put students of this particular branch in a position to follow the lines on which the experiments were carried out.

*Experimental Researches into the Properties and Motions of Fluids, with Theoretical Deductions therefrom.* By W. FORD STANLEY.  
London: E. and F. N. Spon, 1881, pp. 550 + xvi.

"I HAD taken for the amusement of my leisure an experimental examination of the undulatory theory of light, which I could not satisfactorily comprehend. In following up my experiments for two years, I found my eyesight impaired, and was advised that it would be necessary to leave these experiments, and also close application to reading, for some years, which I did very reluctantly. One branch of experiment, somewhat relative to my former studies, however, appeared open to me. The theory of undulation of light was generally introduced to our conception by philosophers by similitudes of the motions of water-waves and sound-waves; I thought I would investigate experimentally, as far as possible to me, to be assured our conceptions of these motions were real, upon inductive principles, similar to those I had been employing for investigation of light. In this subject, taking no preconceived theory whatever for my experiments, I soon became absorbed in observations of the motive effects evident in the directions taken by impressed forces in fluids under various conditions of resistance; wherein it appeared to me quite evident that there was yet an immense amount of work to be done in researches in the motions of fluids, before theoretical principles of the sciences of hydrodynamics and acoustics could be fixed upon mechanical principles with any great precision. It was therefore clear to me that in this direction I might, if I had the ability, enter upon fields of research quite as new as in my former studies."

This quotation will serve a double purpose: it will show that the author's style requires the aid, which he himself states that his book lacked, "of some well-read or well-instructed student" to prune it; and also how the present work has come into existence, in being the record of a very great number of apparently carefully performed experiments.

There is an immense deal of matter, accompanied by numerous plates, which may possibly in skilled hands be worked up, in some future treatise on hydrodynamics, into a more elegant form. In the

meanwhile, Mr. Stanley deserves our thanks for having carried on these researches, and for having, to the best of his ability, put them on record.

It was the author's idea to divide his book into four sections ; the fourth however, on sound-motions in fluids, is for the present kept in abeyance, though we are told that it is written. It would now, of course, have to discuss the recent discoveries of telephones, microphones, phonographs, *et id genus omne*.

The first section treats of theoretical conditions of the fluid state and motive properties of forces in fluids. Here, in the second chapter, Mr. Stanley goes against the theory accepted from Segner to Clerk Maxwell, and takes the view that the surfaces of liquids are *extensile*, and not *tensile*. He, however, modestly enough thinks that he may have insufficiently worked out this subject, "although my experiments in this, as in most other subjects taken, are ten times the number given." Throughout there is the same diffidence. Thus, again, in his eighth chapter, on resistance of solids, he remarks that "it is very incomplete on certain points for want of sufficient research into the works of others, and more experiment ; therefore it may be considered to be in a certain degree speculative."

The fifth chapter discusses the projection of fluids within like fluids, the principles of conic resistance, and planes of fracture and tension. This contains many matters of interest, amongst others the interesting experiments of Tait and O. Reynolds on smoke-rings, with some of the author's own experiments.

The second section is devoted to the discussion of cosmical phenomena ; and herein he follows to some extent ideas put forth by Dr. Carpenter and other writers.

The third section is concerned with waves, experiments on which were made before the writer was acquainted with Scott-Russell's experiments. "As I was working for the demonstration of principles only, I do not regret the want of this knowledge at first ; for if I had possessed it at the time it would have materially curtailed the interest I took in my experiments. . . . I have, however, replaced Mr. Russell's work for my own, where it appeared more demonstrative."

Mr. Stanley has received very little help, except from books, references to which are given throughout ; he, however, warmly thanks Professors Fuller and Stokes for "valuable occasional critical notes" on the earlier portion. The book is well printed and illustrated.

XXXV. *Intelligence and Miscellaneous Articles.*

NOTE ON MR. J. J. THOMSON'S INVESTIGATION OF THE ELECTROMAGNETIC ACTION OF A MOVING ELECTRIFIED SPHERE. BY GEORGE FRANCIS FITZGERALD, FELLOW OF TRINITY COLLEGE, DUBLIN, ETC.

IN the April number of the Philosophical Magazine for the present year Mr. J. J. Thomson has given an interesting investigation of the electromagnetic action of a moving electrified sphere.

On the fourth page (*loc. cit.* p. 232) of this investigation, he makes an assumption, which he does not justify, in order to make the components of the vector-potential of electromagnetic induction satisfy the condition

$$\frac{dF}{dx} + \frac{dG}{dy} + \frac{dH}{dz} = 0.$$

As it seemed very likely that they ought to satisfy this condition, I thought it worth while bringing before the Society a justification of his assumption, which, however, leads to slightly different equations from his, though his final result is unaffected.

Mr. Thomson has not touched the question of the discontinuity at the surface of the sphere, nor what becomes of the displacement when the sphere passes over a point. We may assume that the point remains in its displaced position (and this is practically what Mr. Thomson assumes); but if we do, the above condition is not fulfilled. We may assume that it returns to its original position, so that no permanent displacement takes place in the track of the sphere as would occur on Mr. Thomson's assumption. This, however, does not satisfy the condition either; and I have been led to assume that the particle does return to its original position, but that in some way or other the discontinuity at the surface acts as if a moving quantity of electricity acted like an element of an electric current. This may seem like begging the question; but it is only doing explicitly what Mr. Thomson does implicitly. It is evidently impossible that the electromagnetic action of moving electricity can be due entirely to the electromagnetic action of the displacement-currents in the dielectric; for in the case of a plane moving parallel to itself there are none of these displacement-currents, and yet that is the only case that has been experimentally verified.

To show that my assumption leads to equations satisfying the condition, and leading to practically the same results as Mr. Thomson's, does not require much work.

Consider an elementary volume  $dx ds \cdot \cos \theta$ , where  $ds$  is an element of the surface of the sphere, and  $\theta$  the angle the radius makes with  $x$ . The displacement in this volume is  $=\delta$ , the superficial density, while after the time  $dt$  it is zero on my assumption.

\* From the Scientific Proceedings of the Royal Dublin Society, vol. iii. part 4, having been read November 21, 1881. Communicated by the Author.



Hence calling the displacement  $D$ , we have

$$\frac{dD}{dt} dt = -\delta \cdot dx ds \cdot \cos \theta.$$

Hence

$$\dot{D} = -\delta \cdot \frac{dx}{dt} \cdot ds \cdot \cos \theta.$$

Now  $\frac{dx}{dt} = p$ , the velocity of the sphere which is supposed to be moving along  $x$ . Hence the components of  $\dot{D}$  are  $\dot{f}$ ,  $\dot{g}$ ,  $\dot{h}$ ; and observing that  $ds = a^2 d\mu d\phi$ , where  $\cos \theta = \mu$ , and  $a$  is the radius of the sphere, while  $4\pi a^2 \cdot \delta = e$ , the total quantity of electricity on the sphere,

$$\dot{f} dx dy dz = -\frac{ep}{4\pi} \mu^2 d\mu d\phi,$$

$$\dot{g} dx dy dz = -\frac{ep}{4\pi} \mu \cos \phi d\mu d\phi,$$

$$\dot{h} dx dy dz = -\frac{ep}{4\pi} \mu \sin \phi d\mu d\phi.$$

Hence the components of the electromagnetic potential are at a point at a distance

$$F_s = -\frac{ep}{4\pi} \iint \frac{\mu^2}{r} d\mu d\phi,$$

$$G_s = -\frac{ep}{4\pi} \iint \frac{\mu \cos \phi}{r} d\mu d\phi,$$

$$H = -\frac{ep}{4\pi} \iint \frac{\mu \sin \phi}{r} d\mu d\phi.$$

These are the components of the electromagnetic potential due to this superficial change of displacement that I have assumed. When integrated over the surface of the sphere, they give at a point distant  $R$  from its centre, and whose polar angles are  $\alpha$  and  $\epsilon$ ,

$$F_s = -\frac{ep}{3R} - \frac{epa^2}{5R^3} (\cos^2 \alpha - \frac{1}{3}),$$

$$G_s = -\frac{epa^2}{5R^3} \cos \alpha \cdot \sin \alpha \cdot \cos \epsilon,$$

$$H_s = -\frac{epa^2}{5R^3} \cos \alpha \cdot \sin \alpha \cdot \sin \epsilon.$$

If we add to these the components calculated by Mr. Thomson as due to the external displacement-currents, and given by him (*loc. cit.* p. 233), namely

$$F_e = \frac{ep}{10R^3} (5R^2 - 3a^2) (\cos^2 \alpha - \frac{1}{3}),$$

$$G_e = \frac{ep}{10R^3} (5R^2 - 3a^2) \cos \alpha \sin \alpha \cos \epsilon,$$

$$H_e = \frac{ep}{10R^3} (5R^2 - 3a^2) \cos \alpha \sin \alpha \sin \epsilon,$$

we get, as the resultant values of the components produced by the displacements assumed,

$$F_d = -\frac{ep}{3R} + \frac{ep}{2R^3}(R^2 - a^2)(\cos^2 \alpha - 3),$$

$$G_d = \frac{ep}{2R^3}(R^2 - a^2) \cos \alpha \sin \alpha \cos \epsilon,$$

$$H_d = \frac{ep}{2R^3}(R^2 - a^2) \cos \alpha \sin \alpha \sin \epsilon,$$

which, however, do not satisfy the condition

$$\frac{dF_d}{du} + \frac{dG_d}{dy} + \frac{dH_d}{dz} = 0.$$

Now it is very easy to calculate the action of the superficial moving electricity if it be assumed to act like an electric current. Each element of the surface will act as if it had an electric  $\delta \cdot p$  on it: and the  $x$  components of the electromagnetic potential will evidently be the same as the electrostatic potential, while the  $y$  and  $z$  components will vanish. Hence

$$F_c = \frac{\mu ep}{R}, \quad G_c = H_c = 0.$$

My assumption is that the complete components are

$$F = F_c + F_d, \quad G = G_c + G_d, \quad H = H_c + H_d;$$

and it is easy to see that they can be put into the form

$$F = \frac{\mu ep}{R} + \frac{\mu ep}{6} \left\{ (R^2 - a^2) \frac{d^2}{dx^2} \cdot \frac{1}{R} - \frac{2}{R} \right\},$$

$$G = \frac{\mu ep}{6} (R^2 - a^2) \frac{d^2}{dx dy} \cdot \frac{1}{R},$$

$$H = \frac{\mu ep}{6} (R^2 - a^2) \frac{d^2}{dx dz} \cdot \frac{1}{R};$$

and these satisfy the condition

$$\frac{dF}{dx} + \frac{dG}{dy} + \frac{dH}{dz} = 0.$$

These may be further simplified by assuming a function

$$\chi = -\frac{\mu ep}{2} \left( x + a^2 \frac{d}{dx} \right) \frac{1}{R},$$

$$F = -\frac{\mu ep}{R} + \frac{d\chi}{dx},$$

$$G = \frac{d\chi}{dy},$$

$$H = \frac{d\chi}{dz}.$$

We hence easily see that, in the general case where the sphere is moving with component velocities  $p, q, r$ , we must take

$$\chi = -\frac{\mu e}{z} \left\{ px + qy + rz + a^2 \left( p \frac{d}{dx} + q \frac{d}{dy} + r \frac{d}{dz} \right) \right\} \frac{1}{R};$$

or, calling

$$p \frac{d}{dx} + q \frac{d}{dy} + r \frac{d}{dz} = \frac{d}{d\theta},$$

and observing that

$$p \frac{x}{R} + q \frac{y}{R} + r \frac{z}{R} = \dot{R},$$

we have

$$\chi = -\frac{\mu e}{2} \left( \dot{R} + a^2 \frac{d}{d\theta} \cdot \frac{1}{R} \right);$$

and then we have

$$F = \frac{\mu e p}{R} + \frac{d\chi}{dx},$$

$$G = \frac{\mu e q}{R} + \frac{d\chi}{dy},$$

$$H = \frac{\mu e r}{R} + \frac{d\chi}{dz}.$$

From these it appears at once that the magnetic effect of the displacement-currents is *nil*. For the components of the magnetic forces  $\alpha, \beta, \gamma$  are

$$\alpha = \frac{dG}{dz} - \frac{dH}{dy},$$

$$\beta = \frac{dH}{dx} - \frac{dF}{dz},$$

$$\gamma = \frac{dF}{dy} - \frac{dG}{dx};$$

and  $\chi$  disappears from this, and there only remains the magnetic action due to the current that I have assumed to represent the moving superficial electricity. The effect of this is obviously the same as if the whole quantity of electricity were moving at its centre; and this is the same as Mr. Thomson's result (*l. c.* p. 236).

It is to be observed that Mr. Thomson has intentionally omitted the self-induction of these displacement-currents on one another; and it may legitimately be omitted when the motion is comparatively slow; but a complete solution of the question would be most interesting.

It may be worth while remarking, that no effect except light has ever yet been traced to the displacement-currents assumed by Maxwell in order to be able to assume all currents to flow in closed circuits. It has not, as far as I am aware, been ever actually demonstrated that open circuits, such as Leyden-jar discharges, produce exactly the same effects as closed circuits; and until some such effect of displacement-currents is observed, the whole theory of them will be open to question.

## ON A VIBRATORY MOTION AT THE ORIGIN OF A JET OF VAPOUR.

BY M. TH. VAUTIER.

In the course of some researches which I have commenced upon the flow of gases and vapours, I have observed a singular phenomenon, which was first signalized in 1826, by an engineer of Fouchambault's iron-works:—When a jet of gas or vapour flows, under pressure, through an orifice, if a plate be placed normal to the axis of the jet, at a certain height, it is repelled; but when the plate is lowered parallel to itself, it is attracted, and spontaneously supports itself at about 0·2 millim. from the orifice, oscillating about a position of equilibrium and emitting a sound.

I have succeeded, by means of a very simple arrangement, on fixing some plates in that situation, in making them give forth sounds high, intense, as prolonged as I pleased, and directly register those vibrations. I have obtained in the tracings, undulations of remarkable regularity and amplitude.

I have directly registered the vibrations, thus kept up by a jet of vapour, of a plate giving a note close to the  $la_{\frac{7}{6}} = 7250$  single vibrations per second. An electrodiapason simultaneously registered its vibrations. Pressure in the boiler, 4·5 atm.; diameter of the orifice, 2·7 millim. Diameter of the plate, 6 millim.; thickness, 1·5; distance from the orifice, 0·2; amplitude of the vibrations, 0·7. Thus, then, we have a chronograph directly registering  $\frac{1}{7250}$  of a second.

The sound which I get is intenser than that of the diapasons which give the same note, and of which it has not, up to the present, been possible to sustain the motion electrically in a practical manner, and, consequently, to register it continuously. The apparatus which I have prepared traces, as long as I please, in sharp outline, regular vibrations of sufficient amplitude to be subdivided in the usual manner. This subdivision is facilitated by the fineness of the tracing, which is obtained by means of very sharp styles, which, pressed lightly upon sheets of mica either smoked or not, leave a thin stroke engraved upon those surfaces.

Hitherto, at least to my knowledge, it has been found possible at most to register, directly and continuously, the thousandth part of a second, which is afterwards divided. The apparatus which I use registers directly the seven-thousandth of a second; and the tracing, very thin, favours the usual divisions. The results obtained by me quite recently permit me to expect to register sounds of still higher pitch. I purpose to apply this chronograph to the measurement of some rapid phenomena.—*Comptes Rendus de l'Académie des Sciences*, March 6, 1882, t. xciv. p. 642.

## ON THE COMPRESSIBILITY OF GASES. BY M. E. SARRAU.

1. In a memoir on the compressibility and expansion of carbonic acid, very important when regarded from the thermodynamic point of view, M. Clausius has proposed for this gas the following relation between the pressure ( $p$ ), the volume ( $v$ ), and the absolute temperature ( $T$ ):—

$$p = \frac{RT}{v - \alpha} - \frac{K}{T(v + \beta)} \cdot \cdot \cdot \cdot \cdot \cdot (1)$$

The eminent physicist has verified, with the aid of Andrews's experiments, that this relation represents exactly the transformations of gaseous or liquid carbonic acid; and he thinks that the same formula, with suitable values of the constants  $R$ ,  $K$ ,  $\alpha$ ,  $\beta$ , must be correct for all gases.

Among the consequences resulting from this formula must be noticed those concerning the *critical point*. Indeed it follows, from the interpretation given by M. Clausius of the results of his formula, that when the critical point is reached the function  $p$  satisfies the two conditions  $\frac{dp}{dv}=0$ ,  $\frac{d^2p}{dv^2}=0$ . By combining these conditions with the relation (1) we get three equations, from which we deduce the following values of  $v$ ,  $T$ ,  $p$  corresponding to the critical point:—

$$v_c = 3\alpha + 2\beta; \quad T_c = \left(\frac{2}{3}\right)^{\frac{2}{3}} \left(\frac{K}{R}\right)^{\frac{1}{3}} (\alpha + \beta)^{-\frac{1}{2}}; \quad p_c = 6^{-\frac{2}{3}} (KR)^{\frac{1}{3}} (\alpha + \beta)^{-\frac{3}{2}} \quad (2)$$

2. I proposed to myself to verify M. Clausius's relation for other gases than carbonic acid, making use of the extensive experiments of M. Amagat, in which the temperature varied from  $15^{\circ}$  to  $100^{\circ}$ , and the pressure from 25 to 320 metres of mercury.

The numerical determination of the coefficients being not without difficulties, it is not needless to indicate the course which I have uniformly pursued to accomplish it. Let  $p$  and  $p'$  be the pressures corresponding to one and the same value  $v$  at two different temperatures  $T$ ,  $T'$ ; we have the two relations

$$p = \frac{RT}{v - \alpha} - \frac{K}{T(v + \beta)^2}, \quad p' = \frac{RT'}{v - \alpha} - \frac{K}{T'(v + \beta)^2}.$$

Putting

$$x = \frac{T'^2 - T^2}{p'T' - pT}, \quad y = \sqrt{\frac{T'^2 - T^2}{TT'(p'T - pT')}},$$

we deduce from the above two equations, by successively eliminating  $K$  and  $R$ ,

$$\frac{v - \alpha}{R} = x, \quad \frac{v + \beta}{\sqrt{K}} = y. \quad \dots \dots \dots (3)$$

Therefore knowing two corresponding values of  $v$  and  $x$  suffices for obtaining  $R$  and  $\alpha$ , and two corresponding values of  $v$  and  $y$  for obtaining  $K$  and  $\beta$ ; but if we take a superabundant number of simultaneous values  $(v, x)$  and  $(v, y)$ , we can verify the exactness of the relations (3) and make all the equations contribute to the calculation of the coefficients. M. Amagat's experiments do not give directly the pressures which at different temperatures correspond to the same volume; I obtained them by interpolation. The mode of calculation adopted employs for the values of the coefficients the units employed by M. Amagat. The pressures are expressed in metres of mercury, or, dividing by 0.760, in atmospheres. The unit of volume is not specified; but without knowing this we can determine the values possessed by the constants by taking for unit the volume of the gas under the atmospheric pressure and at zero. In fact, in consequence of the change of unit,  $v$  must be re-



placed by  $\frac{v}{\epsilon}$ ,  $\epsilon$  being a conveniently chosen factor. Relation (1) thus becomes :—

$$p = \frac{R\epsilon T}{v - \epsilon\alpha} - \frac{K\epsilon^2}{T(v + \epsilon\beta)^2}.$$

The volume of the gas under the normal pressure at zero being taken as unit, it follows from the properties of perfect gases that  $R\epsilon$  becomes  $= \frac{1}{273}$ . The factor  $\epsilon$  is therefore determined.

3. *The Compressibility and Critical Point of Oxygen*.—The calculation, applied to two series of experiments on oxygen \*, leads to the following values :—

$$\log R = 1.23676; \quad \log K = 7.08424; \quad \alpha = 4.19; \quad \beta = 3.23.$$

If with these coefficients, and employing measured volumes, we calculate the corresponding pressures, we find the numbers in the following Table, from which the accuracy of the formula can be appreciated :—

Temperature 14°·7.				Temperature 100°·2.			
Pressure.				Pressure.			
Volume.	Measured.	Calculated.	Difference.	Volume.	Measured.	Calculated.	Difference.
	atm.	atm.	atm.		atm.	atm.	atm.
40·90 .....	113·4	113·6	—0·2	45·57 .....	141·1	141·9	—0·8
32·78 .....	141·1	141·1	0·0	35·97 .....	181·1	181·4	—0·3
25·67 .....	181·1	180·5	+0·6	27·52 .....	240·9	241·5	—0·6
19·56 .....	240·9	241·7	—0·8	20·20 .....	342·1	342·8	—0·7
14·59 .....	342·1	344·3	—2·2	17·16 .....	418·9	418·1	+0·8
12·74 .....	418·9	414·8	+4·1				

Adopting for the unit of pressure the atmospheric pressure, and for the unit of volume the volume of the gas at zero under the pressure of the atmosphere, the four constants of the formula are, for oxygen,

$$R = 0.003663, \quad K = 0.5475, \quad \alpha = 0.000890, \quad \beta = 0.000686;$$

and for the critical point the values of the variables, calculated by the formulæ (2), are

$$v_c = 0.004042, \quad t_c = -105^\circ\cdot4, \quad p_c = 48\cdot7 \text{ atm.}$$

These numbers lead to a remarkable consequence. M. Raoul Pictet measured the density of solid oxygen at the temperature of about  $-110^\circ$ , under the pressure of 470 atmospheres. If we seek, by means of the formula, the corresponding value of  $v$ , we find 0.00136. Applying this result to the unit of weight, and taking the litre as unit, we find  $0.00136 \times 697.2 = 0.948$ . The density, therefore, is very close to unity, in accordance with the valuation of M. Raoul Pictet. In an early communication I will make known the results relative to the other gases investigated by M. Amagat. — *Comptes Rendus de l'Académie des Sciences*, March 6, 1882, t. xciv. pp. 639–642.

\* *Comptes Rendus*, Nov. 15, 1880.

THE  
LONDON, EDINBURGH, AND DUBLIN  
PHILOSOPHICAL MAGAZINE  
AND  
JOURNAL OF SCIENCE.

[FIFTH SERIES.]

MAY 1882.

XXXVI. *Physiological Perspective.*

By W. LE CONTE STEVENS\*.

[Plate VIII. figs. 1-5.]

1. *Brewster's Experiment.*

SIR DAVID BREWSTER, in his essay 'On the Knowledge of Distance given by Binocular Vision' (1844), and in his subsequent volume on the Stereoscope (1856), describes the binocular union, by optic convergence, of similar pictures regularly recurring on large surfaces. The result of viewing, by cross vision, flowers twelve inches apart, on a papered wall at three feet distance, he describes partially as follows†:—"The whole papered wall, with all its flowers, will be seen suspended in the air at the distance of six inches from the observer. At first the observer does not decide upon the distance of the suspended wall from himself. It generally advances slowly to its new position; and when it has taken its place it has a very singular character. The surface of it seems slightly curved."

The geometric explanation of the position of the phantom wall, as given by Brewster‡, is easily understood. Let R and L (fig. 1) be the optic centres of the right and left eyes respectively, and A, B, C, A', B', C', equidistant points on the wall. If the right eye is directed to A and the left to A', the intersection of visual lines is at *a*. The points *b* and *c* are determined in like manner; and if the interocular line

\* Communicated by the Author.

† Brewster on the Stereoscope, London, 1856, p. 91.

‡ *Ibid.* p. 95.

R L be parallel to the wall, it follows that the phantom surface must be a plane  $S S'$  parallel to the wall. This explanation fails to account for the apparent curvature  $S'' S'''$ ; and on actually trying the experiment it will be found that the convexity is very slight unless the optic convergence be strong.

## 2. *The Binocular Eye.*

In examining this phenomenon it is indispensable that the observer distinguish between subjective effects and objective realities, between a sensation and its exciting cause. In seeing with two eyes, the sensation is the same as if both were fused into a single binocular eye, midway between them, whose optic centre is the point of origin in all estimates of direction and distance. The two visual lines are subjectively combined into a single line, extending from the yellow spot of the binocular eye as far as the external point to which the observer mentally refers the combined retinal picture. There can hence be no perceived intersection of visual lines as assumed by Brewster. The recognition of optic convergence or divergence is through the muscular sense; and the localization of objects in the field of view is the interpretation of a complex sensation, not a simple geometric determination. I have recently devised a refracting stereoscope\*, by means of which the same stereograph, within a few seconds of time, may be viewed successively by optic divergence, with natural relief, and by slightly greater convergence with reversion of relief. The binocular image is seen either alone or accompanied by a pair of monocular images, as may be preferred, and varies in apparent distance and size according to the degree of muscular strain attendant upon binocular vision in each case. The appearance of monocular images can be easily secured with the ordinary lenticular stereoscope, by removing the longitudinal screen while the relation between the two visual lines is kept unchanged. The subjective effect is that the binocular image, in full relief, remains apparently single and directly in front of the binocular eye, while on each side of it a separate monocular image is perceived by indirect vision. This is true for optic divergence as well as convergence; and the recognition of the subjective union of the eyes must underlie any attempt to explain the phenomena of binocular vision.

## 3. *Gradation in Retinal Fusion.*

However mistaken Brewster may have been in his theory

\* American Journal of Science, March 1882.

of visual triangulation, he was right in laying stress upon the successive changes of relation between the visual lines in attaining the illusion of binocular relief. In many cases this is indispensable to perfect success; but it is not a fully sufficient explanation. When the stereoscopic displacement on the conjugate pictures is small, the perception of relief is instantaneous, as has been abundantly established by the experiments of Dove, Helmholtz, Le Conte, and others, who illuminated the stereograph with the electric spark. But when the stereoscopic displacement is large, if a pair of properly constructed diagrams be employed, the superposed external images may be made apparently to spring into full relief only by play of the eyes, and to flatten out into a confused network of intersecting and partially coalescent lines by making the gaze rigidly fixed. The perception of relief is then confined to those parts where the displacement is small. The fact that this residual relief is always more or less perceptible, indicates that the generally accepted theory of corresponding retinal points cannot be interpreted mathematically. The so-called *minimum visibile* is not a point, but corresponds to a retinal area whose diameter is variously estimated from .003 mm. to .005 mm. It is impossible to perceive separately an object whose retinal picture is smaller than this. But it may be quite possible for the *quality* of a retinal sensation to be modified while the additional impression, apart from that which it modifies, would be imperceptible. This indeed is quite comparable to our perception of musical quality by the ear. Through the auditory nerve it has always been possible to distinguish between notes of the same fundamental pitch from different sources. It was reserved for Helmholtz to analyze by instrumental aid what had previously eluded analysis by the unaided ear, and show that minute modifications upon the sensations that had been regarded as identical were due to additional impressions that were separately imperceptible without resonators. The sensible coalescence between a fundamental and the overtones which give it character, or between the sensations produced by two well-trained unisonant voices, each with its attendant overtones which make them produce slightly dissimilar sound-images, is in no way more remarkable than the sensible coalescence of slightly dissimilar light-images, with the production of new and recognizable quality. Whether the complete analysis of such complex images will ever be made is for the future to develop.

Wheatstone therefore was correct in his theory of mental fusion of retinal images, so far as this goes; but it does not

go far enough. Brewster was right in considering it inadequate, and emphasizing the fact that while the foreground is seen single the background must be double; but the qualifying statement is necessary that this is perceptible only when the stereoscopic displacement is considerable. Returning to the comparison with sound-perceptions, two strings of different material may be mistuned so as to produce beats; but by successive alterations of tension they may be made sensibly unisonant, with alternately higher and lower pitch, yet the resultant quality in each case is perceived to be different from that of the sound from either string alone. In like manner, with retinal sensations, we may pass from sensible coalescence with distinctions of relief in the foreground, while the background is double, to similar coalescence in the background, leaving the foreground double. The simultaneous relaxation of muscular tension produces the impression of greater distance of the new points thus combined by modified fusion; for in normal binocular vision the internal rectus and ciliary muscles become relaxed in withdrawing the attention from a very near body and bestowing it upon one that is distant.

#### 4. *Physiological and Physical Perspective.*

Wheatstone and Brewster thus separately emphasized the importance of phenomena that are complementary, not contradictory. Wheatstone's theory of binocular perspective was based mainly upon physiological considerations; and he indicates that he regards convergence of visual lines as invariably accomplished in all binocular vision, though he cites some exceptional cases in which it seems not to determine the apparent position of the object viewed. Brewster's theory was distinctively geometric; he considered variation of relation between visual lines to be important because the successive points in the field of view were to be *determined* by their intersection; and hence he concludes that "we see distance."\* Subsequent investigation now proves that the localization of what is viewed in the stereoscope is in no way dependent upon such intersection, but that binocularly we simply estimate distance as in monocular vision. The estimate is indeed for short distances far more definite, in both normal and stereoscopic vision, than when a single eye is employed, because the muscles of the two eyeballs are called into associated action, independently of the sensible coalescence of slightly dissimilar retinal images in the binocular eye. Certain muscular contractions are habitually associated with certain motions of the body viewed, or certain relations between its different parts.

\* Brewster on the Stereoscope, p. 50.



If the binocular examination of the stereograph necessitate these contractions, the corresponding judgment which follows is dependent upon the observer's ability to interpret nerve-impressions, muscular as well as retinal, and not on the mathematical relation between his visual lines. For the apparent relation between objects in the binocular field of view, as influenced by the temporary condition of the muscles of the eyes, I have proposed the name of physiological perspective\*, in contrast with what is suggested by the ordinary elements, whose total effect may be called physical perspective. The judgment suggested by the former may either coincide or conflict with that suggested by the latter. The result is either enhancement, or partial reversion, or total reversion, according to the arrangement of conditions. The convexity of the spectral wall which Brewster observed, and which is inexplicable on his theory of visual triangulation, is an illustration of both physiological and physical perspective; and by varying the conditions reversion is easily produced. In discussing it, any reference to corresponding retinal points must be understood in the modified sense already explained, and not mathematically.

#### *5. A New Mode of Stereoscopy.*

Brewster's experiment may be performed more satisfactorily by constructing on cardboard a pair of perfectly similar figures, each consisting of a series of concentric circles. Combining the images of these by bringing the card quite near and crossing the visual lines at an angle of at least  $60^\circ$ , the binocular image appears suspended in mid air, diminished in size, more especially so in a direction parallel to the interocular line, but convex toward the observer, to whom the appearance is that of a miniature elliptic buckler. The experiment is quite straining upon the muscles of the eyes. A far easier method is to cut the card across at the middle, and incline the two halves so that at the edges in contact the two faces shall form a dihedral angle of  $120^\circ$ , or less, opening toward the observer. If the interval between the two centres be equal to the observer's interocular distance, or slightly exceed this, he may easily secure binocular combination with the visual lines parallel or divergent; and the convex shield is seen, larger than in the previous experiment, and sensibly a little more distant than when either picture is viewed separately as in ordinary vision. If there be difficulty in relaxing the muscles of the eyes sufficiently, the cards may be properly held in front of the semi-lenses of an ordinary

\* American Journal of Science, Nov. 1881, p. 361.

stereoscope, though vision with the unaided eyes is preferable. The visual result is thus obtained without strain, and by optic parallelism or divergence, either of which conditions makes Brewster's theory of intersection inapplicable. By reversing the inclination of the cards to the parallel visual lines, the apparent convexity is changed into concavity. We have thus stereoscopy obtained from a pair of perfectly similar conjugate pictures, and capable of reversion at will without conscious motion of the eyes or removal of the stereograph.

This is, so far as I have been able to learn, a new phenomenon in binocular vision. Brewster's unexplained observation had apparently passed into oblivion on account of the exceeding strain upon the eyes which it involved. The curvature of the phantom wall, in a plane passing longitudinally through the observer's body, has lately been rediscovered by Professor Joseph Le Conte, and shortly afterwards its curvature in all directions by myself. On working out the explanation, which would not have been possible except by rejecting Brewster's theory of triangulation, I at once devised a simple attachment for my adjustable stereoscope, capable of use however with any such instrument, if so arranged that the stereograph may be rested upon a cross bar, instead of sliding within a box. Let MN (fig. 2) be such a cross bar, in front of the eyes whose optic centres are at O and O'. A pair of extra short bars PQ and P'Q' are pivoted at C and C', over which rest the centres of two similar series of concentric circles whose horizontal diameters are included between E and D, E' and D', respectively, the plane of each card being perpendicular to the page. The central visual lines CO and C'O' are parallel, but for obvious reasons made very short in the diagram. The retinal projections of ECD and E'C'D' are *ecd* and *e'c'd'* respectively. Because the triangles EOD and E'O'D' are oblique, their medians divide the angles at O and O' unequally; hence  $dc > ce$  and  $d'c' < c'e'$ . The retinal images in the two eyes are hence dissimilar; and this dissimilarity may be made so great by increasing the angles NCD and MC'E', that the binocular image becomes indistinct if the eyes are not made to play rapidly over the picture. If the attention be momentarily withdrawn from C and C' to D and D', the visual lines become divergent to an extent measured by the difference of the angles  $d\hat{O}c$  and  $d'\hat{O}'c'$ . The associated contraction of the external rectus muscles which this necessitates, at once produces the sensation that habitually accompanies recession of the object binocularly viewed. The same is true if the attention be restored to C and C', and then given to E and

E'. The binocular image of the horizontal diameters must hence be perceived as a curve, convex toward the observer.

Each circle, obliquely viewed, must be seen approximately as an ellipse, the ratio of whose axes is readily calculable if the angle of inclination be known. But the retinal ellipses are no longer concentric (figs. 3 and 4), the extent of retinal displacement depending on the extent of minor axis in each. If the successive vertices be connected, we have two curved lines,  $ACB$  and  $A'C'B'$ . If these be binocularly combined and externally projected, since  $C'C$  is less than  $A'A$  and  $B'B$ , optic divergence becomes necessary in transferring the attention from  $C$  and  $C'$  to  $A$  and  $A'$  or  $B$  and  $B'$ . The binocular image of the vertical diameters must hence be perceived as a curve convex toward the observer.

Let  $F$  and  $G$  (fig. 3) be points symmetrically situated with regard to the vertical diameter, and hence equidistant from  $D$  and  $E$  respectively. When the card is revolved, as in fig. 2, the distance  $OE$  exceeds  $OD$ , and hence the visual angle subtended by  $EG$  is less than that subtended by  $DF$ . Every ellipse therefore is distorted; but since the distortion is equal and opposite on the two retinas, it is perfectly corrected in the binocular combination of each pair of curves. To each eye separately the effect is the same as if every major axis were bent, and every point of each curve, above and below the horizontal axis, were correspondingly displaced:  $F$  and  $G'$  are elevated,  $F'$  and  $G$  depressed; hence  $F$  and  $F'$  differ in retinal latitude as well as longitude, but are nevertheless binocularly combined. This confirms the views of Wheatstone in opposition to those of Brewster.

If a pair of small circles whose vertical diameters are  $ab$  and  $a'b'$  be viewed above the large circles, the visual lines directed to their centres are similarly oblique to their vertical diameters. They are therefore retinally projected as approximate ellipses; and when these are thence externally projected, their upper vertices are further apart, and their lower vertices nearer together, than their centres. The binocular combination is hence an ellipse whose plane is oblique, the upper vertex being further from, and the lower vertex nearer to, the observer. A pair of small circles below the large ones are binocularly combined with opposite obliquity.

No explanation is now needed to show that if the planes of the cards be revolved into the positions  $P''Q''$  and  $P'''Q'''$  (fig. 2), the binocular combination of the concentric circles must present a concave surface, and the obliquity of the plane of each pair of conjugate small circles, when binocularly viewed, must be reversed in sense.

Brewster's remark about the phantom wall, that "it generally advances slowly to its new position," is now easily understood. At that time the nature of focal adjustment by action of the ciliary muscle in each eye was not known. When  $E$  and  $E'$  (fig. 2) are binocularly viewed, since  $EO$  exceeds  $E'O'$ , there must be dissociation between the two focal adjustments which are generally adapted to the same distance. To this must be added the necessary dissociation between axial and focal adjustments, the former being for an infinite distance, the latter for the distance  $OC$ , when  $C$  and  $C'$  are binocularly viewed. To untrained eyes this unusual muscular action is not always easy, and cannot be secured without effort that may consume several seconds of time. The result is momentary confusion; and many persons are hence unable to decide at first whether the surface appears convex or concave. Despite these difficulties, the image soon becomes clearly defined when the experiment is performed with axial parallelism. With strong axial convergence, as in Brewster's experiment, the dissociation is far more difficult, on account of the extreme muscular tension made necessary.

#### 6. *The Theory of Associated Muscular Action.*

The theory of visual triangulation seems to have been first put forth in 1604 by Kepler\*, who said that the distance between the two eyes is the base which we employ in measuring the distance of objects, that in so doing we learn to estimate distances with a single eye, and hence that the magnitude of a heavenly body as perceived in the eye would serve as a base for distances relatively slight. Brewster†, in opposition to Berkeley‡, elaborated the idea still further, making it the foundation of his theory of the stereoscope, which has kept its place in our textbooks of Physics to the present day. The retention of this theory, in the face of facts to the contrary, is explicable only in consideration of the circumstances attendant upon normal binocular vision, and the great authority attached to Brewster's views on account of his discoveries as a physicist. Probably neither he nor his followers undertook to ascertain whether the limit of optic parallelism was ever passed in the actual use of the stereoscope. In 1861, two Germans, Rollet and Becker§, published a mode of securing binocular fusion of similar images with the visual lines slightly diver-

\* *Paralipomena*, 1604, pp. 62-66.

† Brewster on the Stereoscope, p. 50.

‡ 'An Essay towards a New Theory of Vision': Dublin, 1709.

§ *Wiener Sitzungsberichte*, May 10, 1861, xliii.; or Helmholtz, *Optique Physiologique*, p. 827.

gent, the possibility of this having been already mentioned by Burckhardt\*, but with no reference to the possibility of stereoscopy from these similar pictures. In 1862, Brewster's theory was criticised by Professor C. F. Himes, of Pennsylvania, who described his experiments in stereoscopy from dissimilar pictures with optic divergence, and called attention to the necessity of modifying the current theory†. Helmholtz related experiments in optic divergence‡, but, unfortunately, did not enter fully into an analysis of the visual results. My own attention was drawn to this subject by the discovery of my power to secure stereoscopy with the unaided eyes by voluntary optic divergence. In a paper read before the New-York Academy of Sciences on the 6th of June 1881, I rejected Brewster's theory; and the phenomena which he had explained by visual triangulation I referred to the associated action of the muscles of the eyes, applying this to both convergence and divergence. It has been very gratifying, therefore, to find my views confirmed by Brigade-Surgeon Tyler Oughton, A.M.D., in two able articles published in the London 'Lancet,' of October 22 and December 31, 1881. These articles were quite independent of my own, each writer having been unknown to the other. In 1877 Mr. Oughton had referred certain phenomena of "erect vision" to the sensation of muscular contraction. My experiments in stereoscopy with perfectly similar pictures, by optic convergence, parallelism, or divergence, with direct or inverse relief at will—experiments capable of ready accomplishment by any one with untrained eyes—still further show that there is no longer any room for the application of geometry to the physiology of vision, beautiful and tempting as may be the theory of visual triangulation.

It is but due to add that the theory of associated muscular action in relation to the stereoscope was virtually stated by Professor Huxley§ in 1868, and in such a way as quite plainly to indicate its applicability to the phenomena of optic divergence. That he did not elaborate it in refutation of Brewster's theory was probably due to the fact that the fallacy and wide spread of this theory had not been brought specially to his attention.

\* *Verhandlung. d. naturforsch. Ges. zu Basel*, i. p. 145; or Helmholtz, *Opt. Phys.* p. 827.

† *American Journal of Photography*, September 1, 1862; also *British Journal of Photography*, 1864.

‡ *Optique Physiologique*, pp. 616 & 828; also 'Popular Lectures on Scientific Subjects,' p. 307 (transl. 1873).

§ 'Elementary Physiology,' p. 286 (Macmillan and Co.).



### 7. *Voluntary Control of the Focal Adjustment.*

Experiments in stereoscopy sufficiently show the office of the rectus muscles in modifying the interpretation put upon retinal sensations. If the visual lines be kept as nearly parallel as possible, and the observer's distance from an object regarded be kept constant, the retinal sensation may still be modified by direct voluntary contraction of the ciliary muscle. It is accompanied by contraction of the pupillary opening; and this can be approximately measured by an assistant. The experiment is straining, but can be performed with very little associated contraction of the rectus muscles. Within two seconds of time the pupillary opening of my eye has thus been often changed to one tenth of its previous area, the contraction of the iris quickly following that of the ciliary muscle. The visual effect is first a slight enlargement of the retinal image as it grows dim; this is due to the production of diffusion-circles, which encroach upon the surrounding retinal area as well as upon the image. The object then apparently diminishes in size to a marked extent. As its absolute distance and diameter, however, are constant, the retinal image cannot be diminished except by encroachment of diffusion-circles. The apparent diminution is far greater than can be explained on this ground, and can only be referred to an error in judgment induced by abnormal muscular conditions that have been voluntarily imposed. The experiment has been many times repeated; and the uniformity of results leaves no room to attribute the illusion to accidental circumstances. The apparent distance of the object to which the gaze is directed becomes indeterminate. Ciliary contraction suggests the idea of its nearness; but the dimness resulting from imperfect focalization suggests its remoteness. The impression of its contraction in area is unmistakable and striking. Since the contractions of the ciliary and internal rectus muscles are usually associated in normal vision, the considerations just expressed explain why so acute an observer as Wheatstone\* should have noticed the apparent decrease in size of the image when strong convergence of visual lines was produced by pulling forward the arms of his reflecting stereoscope, but failed to note the corresponding variation in apparent distance; though he observes that it seems changed in position, but does not say whether the change is that of increase or decrease of distance.

### 8. *Effect of varying the Locality of the Image.*

When strong muscular tension is voluntarily induced, the modification of retinal sensation seems to be greatest at the

\* Philosophical Magazine, 1852, pp. 507 & 508.

yellow spot, and to diminish toward the margins. Let a pair of circles, A and A' (fig. 5), be drawn, a few inches apart, and below A a third circle, A'', equal to each of the others. Bringing the face as near to the page as is consistent with distinct vision, let the right eye be directed to A' and the left to A. A diminished elliptic binocular image is seen directly in front, apparently in mid air; on each side of which is a monocular image, sensibly circular, or but slightly elliptic, distinctly larger than the binocular image, but smaller than either circle seen by normal vision. Even though distinct vision is attained under these conditions, the ciliary muscles are strongly contracted, consensually with the internal rectus muscles. On closing the right eye, relaxation follows, while the direction of the visual line for the eye remaining open is easily kept unchanged. The right monocular image disappears; the elliptic image apparently recedes and moves to the right, growing larger in doing so; but an interval of one or two seconds may elapse before normal monocular vision is restored, and now both circles have recovered their original size. The experiment is very easy.

This process can be reversed, and made as gradual as is desired, by slowly increasing the convergence of visual lines and carrying it beyond the point necessary for binocular combination. As soon as double vision is produced, the two interior images are perceived to be smaller than the exterior ones. They continue to grow steadily smaller and apparently nearer to the observer, until they coalesce in front; but the diminution continues after they have been made to pass each other. On the usually accepted theory, the apparent contraction is referred to the illusive estimate of diminished distance determined by the crossing of the visual lines at the moment the binocular combination is secured. But the falsity of this is additionally shown by regarding the circle A'' while A and A' are binocularly combined. Although necessarily seen only monocularly with each eye, the left-eye image appears directly under the binocular image and of the same size, being much smaller than the right-eye image, which appears under the corresponding one of A.

### *9. Physiology of Retinal Sensation.*

These experiments, taken in connexion with those on stereoscopy, conclusively show that not only is convergence of visual lines not necessary for binocular vision and for the localization of objects in the field of view, but that even change in such localization and in apparent magnitude can be secured without binocular fusion, as a consequence of muscular tension

alone. They indicate a closer relation between the nerves of the ciliary muscle and those of the retina than has been commonly supposed. Through the sympathetic system of nerves the mere action of light on the retina excites reflex muscular contraction of the iris. Without the agency of light, this may be effected by ciliary contraction alone. It is by no means impossible that through this same sympathetic system the impression conveyed to the brain may be modified by such muscular contraction, while the retinal area impressed remains unchanged. The interpretation is unconscious and independent of the will; it is dependent upon the excitement of several different nerves. The thing interpreted is the product of forces from without that operate in accordance with well-known mathematical laws. The velocity of propagation of a nerve-impression has been approximately determined by Helmholtz; but beyond this there has been little success in bringing the physiology of sensation within the domain of mathematics.

That the interpretation of retinal impressions should be more readily modified by association with muscular action when they are produced upon central rather than marginal portions of the retina, is entirely in accordance with the empiristic theory, which Helmholtz, Brücke, and other German physiologists have upheld. In all ordinary vision the attention is habitually given almost exclusively to objects corresponding to retinal images on or near the yellow spot. If any conditions are imposed that tend to induce misinterpretation of our sensations, it might be expected that the most sensitive parts of the retina would be most affected. It is impossible to prove that there is any peculiar necessary relation between the nature of a retinal sensation and the distance of the object pictured, or any innate power to recognize distance. Visual experience begins in infancy, long before the power to analyze sensations; and, in our interpretation of these, association is the chief determinant. Strong ciliary contraction is habitually, though unconsciously, associated with nearness of the object viewed; and this is pictured upon or very near the yellow spot of the retina. No one whose eyes are perfectly healthy has any consciousness of possessing a retina except in relation to external objects of sight, or a ciliary muscle except in relation to variation in distance of the point upon which attention is fixed through the medium of a simultaneous retinal sensation. We might expect, therefore, that unusual muscular conditions would cause misinterpretation regarding the whole field of view, but especially those parts which correspond to the central portion of the retina. This reasoning

applies to variations resulting from tension in the rectus muscles, external and internal, as well as from ciliary change.

### 10. *Binaural Audition and Binocular Vision.*

The discoveries in relation to binaural audition, made during the last few years independently by Professor Silvanus P. Thompson\*, of England, and Professor Alfred M. Mayer†, of this country, are interesting, not only as additions to our knowledge of physiological acoustics, but also in connexion with the phenomena of physiological perspective. The localization of sounds has been found to be much affected by the mode in which the waves are conveyed to the separate ears. The same tone may be perceived as coming from the back of the head, or from the two sides, or from a point obliquely in front, while the position of the true source is unchanged—the perception being involuntary, while the conditions are adjusted at will. The judgment of distance by the ear is far more uncertain than by the eye, there being no criterion other than intensity of the sound perceived; but the perception of direction may be modified by imposing unusual physiological conditions, such as fatiguing one ear with a given tone and then listening to the same with both ears. For a fixed position of the eye, the perception of direction may be modified by changing the medium or pressing upon the eyeball; while that of distance is subject to variable physiological conditions, largely controllable by the will. Although the binaural estimate of direction and distance may be made less uncertain by properly adjusting the position of the head to the wave-fronts of the successive vibrations, no one has attempted to apply geometry to the localization of sounds through binaural audition. Brewster's attempt to do this for binocular vision was based upon two assumptions, each of which has been proven incorrect. The first was, that "the line of visible direction does not depend on the direction of the ray, but is also perpendicular to the retina"‡. The latter clause has been disproved by Helmholtz§. The second was, that convergence of visual lines is necessary in binocular vision, whether normal or stereoscopic||. The falsity of this has been abundantly shown by recent experiments, in addition to those of Burckhardt, Himes, and others. A third fundamental statement by him was, that "distinct vision is obtained only on one point of the retina"¶. While this opinion is still supported by many, it is incapable

\* Philosophical Magazine, Oct. 1877, Nov. 1878, and Nov. 1881.

† 'Researches in Acoustics.'

‡ Brewster on Optics, p. 246.

§ *Optique Physiologique*, p. 93.

|| Brewster on the Stereoscope, pp. 90-106.

¶ *Ibid.* p. 50.

of strict mathematical interpretation. His theory of visual triangulation is inaccurate at best, and almost totally inapplicable in the very department to which it has been most applied—that of stereoscopic perspective.

40, W. 40th St., New York,  
February 24, 1882.

XXXVII. *An Adjustable and Reversible Stereoscope.*

By W. LE CONTE STEVENS\*.

[Plate VIII. figs. 6 & 7.]

THE experiments which formed the basis of my recent papers on Physiological Optics† were, for the most part, made without the aid of any stereoscope, except the modification of Wheatstone's reflector, with which various values of the optic angle were measured. As few persons, however, have sufficient muscular control over the eyes to test my results, I devised an instrument which renders possible for untrained eyes quite a number of experiments which with the ordinary lenticular stereoscope would be either difficult or impossible.

The principal objects to be attained were as follows:—

I. To secure ready motion to the semi-lenses, so that they may be adapted in position for any pair of eyes, whatever may be the distance between the pupils, and for any stereograph, whatever the interval, within the usual limits, between corresponding points on the two pictures.

II. To secure the possibility of removing the semi-lenses at will, so that they may be reversed in relative position, or be replaced by prisms with their bases turned toward each other, so that, without uncomfortable muscular strain, the left picture may be viewed by the right eye and the right picture by the left eye simultaneously, thus producing reversion of relief in the binocular image, if desired.

III. To secure ready motion to the screen, so that to each eye either the whole stereograph, or its right half or its left half separately, may be visible.

IV. To secure the means of examining the binocular image either alone or attended by monocular images, so that the difference between the two kinds of vision may be noted.

V. To secure the means of using the same instrument either with glasses or for binocular combination of images by direct

\* Communicated by the Author.

† Proceedings of the American Association for the Advancement of Science, Cincinnati Meeting, August 1881; Transactions of the New York Academy of Sciences, Oct. 24, 1881, and Feb. 12, 1882; American Journal of Science, November and December 1881; Philosophical Magazine, December 1881.



vision, and to reduce to the utmost the difficulty usually attendant upon stereoscopic vision by the latter method.

VI. To secure the means of producing stereoscopy from perfectly similar pictures, by making the retinal images of these dissimilar by oblique vision.

It gives me pleasure to acknowledge my indebtedness to Messrs. E. and H. T. Anthony and Co., of this city, for every facility that could be asked in testing such devices as presented themselves to my mind; and the form finally adopted gives entire satisfaction, the instrument being compact, inexpensive, and easily managed.

The semi-lenses, *l, l* (fig. 6), instead of being cemented to wood or brass, are gently pressed into a pair of boxes, in the opposite walls of which square openings have been cut to transmit the light from the stereograph, which is held on the cross bar, *a*, by pressure between a pair of brass springs, and may be adjusted to any desired position by sliding this along the longitudinal bar. A pair of adjusting-screws, *s, s*, come into contact with the bases of the semi-lenses, and are opposed by a pair of springs, against which the thin edges press. If the semi-lenses are thus pushed together as near as possible, the rays which enter the observer's eyes pass through the thicker parts, and hence are but little deviated. If they be as far apart as possible, the increase of deviation makes it convenient to employ a stereograph on which the interval between corresponding points is greater than on those generally prepared. This interval is ordinarily limited to about three inches. The focal length of the semi-lenses being seven inches, it has been found that a stereographic interval of four inches can be allowed without any very objectionable coloration due to lack of achromatism, the visual lines of the observer being now parallel or slightly divergent. This divergence may be increased to any extent that he is willing to endure, by turning the adjusting-screws, so as to press the semi-lenses closer together. Binocular fusion of images is thus retained; but the associated contraction of the external rectus muscles produces the illusion of slight recession of the object viewed and increased depth of relief. Similar effects may be obtained by using conjugate pictures separated by the ordinary stereographic interval; but they are much less noticeable, because there is less disturbance of the ordinary condition of the muscles.

In front of the partition between the lens-boxes is hinged a pair of narrow brass screens, *c, c*, which, in the experiments just described, are pressed flat as in fig. 6. The left picture is thus hidden from the right eye and the right picture from the left eye. By folding them together, as in fig. 7, neither

picture is hidden by them from either eye. There is a second sliding cross bar, to which is attached by hinges a light wooden screen, *bb*, which in the same experiments is pressed down, as in fig. 6. By lifting this, as in fig. 7, the opening at the middle leaves the left picture visible to the right eye while the right picture is hidden from it; and *vice versâ* for the left eye. The semi-lenses may now be taken out; and for them are substituted a pair of prisms, *p, p* (fig. 7), whose refracting-angle is  $12^{\circ}$  or  $15^{\circ}$ . The bases of these are pressed against the springs. The cross bar on which the stereograph rests (*a*) is pushed back to the end of the longitudinal bar; and on looking through the prisms the binocular image is seen in pseudoscopic relief. This effect is very striking if the stereograph selected be one in which ordinary perspective is not strong; that of the full moon has been found best. The cross bar may now be pulled as near as convenient, the visual lines becoming more convergent, but not uncomfortably so. Folding down the wooden screen (*bb*), a pair of monocular images of the moon are seen, one on each side of the concave binocular image, but themselves presenting no relief. They appear very perceptibly larger than the binocular image, but slightly smaller than either picture when viewed with normal vision over the stereoscope. Since the prisms have no magnifying- or diminishing-power, this illusion cannot be referred to the effect of refraction, but is explicable only on physiological grounds.

By removing both prisms and semi-lenses the instrument becomes a direct-vision stereoscope, for use with the unaided eyes. To secure natural perspective, arrange the screens as in fig. 6, but push the cross bar as far off as possible. By now gazing, as if through the stereograph at a very distant point, with the muscles of the eyes perfectly relaxed, double vision results, and the two interior images are seen to overlap and then coalesce. For most persons this experiment is difficult if the stereographic interval much exceeds the observer's interocular distance, and it is not at first easy to secure enough muscular relaxation. Some have found it better to draw the cross bar up as near as possible, and then push it off after coalescence of images has been attained, the binocular image being at first very dim.

To secure the pseudoscopic effect by direct vision, arrange the screens as in fig. 7, but push each of the cross bars out as far as possible. Fix the gaze upon the projection (*a*) at the top of the opening in the wooden screen, and keep it thus fixed while the latter is pulled nearer. When this almost reaches the position *bb*, in fig. 7, the interior images beyond

will be seen to coalesce; and the attention can then be transferred to their resultant combination. This is a hemispherical lustrous cup, if the stereograph be that of the moon, which is smaller and nearer than that obtained by use of the prisms. By pulling the cross bar nearer, the cup becomes smaller, relatively shallower, and, for obvious mathematical reasons, elliptic with the minor axis horizontal. The wooden screen can now be folded down, as before, and attention be given to the variable size of the image as determined by the conditions under which it is seen.

The semi-lenses may be restored, and the screens arranged as in fig. 6. The cross bar, *a*, is removed; and in its place is put one upon which are pivoted a pair of revolving bars, whose springs hold in position a pair of cards on which are perfectly similar outline figures, such as series of concentric circles. The production of stereoscopic effects, either orthoscopic or pseudoscopic, at will, by oblique projection upon the curved surfaces of the retinas, has been already fully discussed\* and now needs no explanation.

40 W. 40th St., New York,  
February 27, 1882.

### XXXVIII. On *Pseudo-Carbons*.

By C. F. CROSS, *B.Sc.*, and E. J. BEVAN†.

THERE is a general knowledge amongst chemists that the term "carbon" has been loosely applied to a number of substances whose composition and properties, on the experimental side, and the consideration of the condition of whose formation, on the theoretical side, completely prove their non-elementary nature. Notwithstanding this, a glance at the most modern text-books will show that *coal* is still spoken of as "a form of carbon;" *charcoal* also; and the action of sulphuric acid on sugar is still taught to consist in the resolution of the *carbohydrate* into carbon and water‡, the *dehydrating* energy of sulphuric acid being the efficient cause. It is necessary therefore that these defects in our terminology and classification should be stated, in order that they may be removed. In reviewing this subject we would first account for the existence of the errors in question. Certainly the cause would seem to lie in the inertia of the chemical mind—a desire to *know* without *ascertaining*, a tendency to accept a simple

\* See the preceding article.

† Communicated by the Authors.

‡ This explanation may be dismissed without discussion.

hypothesis framed upon similitudes, and to forsake the rigid requirements of the experimental method where it offers a vista of complexity and the higher mathematics. But perhaps we ought rather to regard the errors in question in the light merely of a confession of postponement of a problem which the science has not yet been in a position to attack, or in favour of the larger number of those more immediately pressing. Still we cannot avoid the conclusion that this has been rather thought than expressed, at least in writing; and whatever be the cause, the persistent use of the terms of which we are speaking amounts to a really grave error. At the outset, therefore, we would propose the term *pseudo-carbons* for the black substances, containing a more or less high percentage of carbon, which are formed in various modes of resolution of the carbon compounds,—including thereby the *coals* and *graphites* of “natural” origin, the *charcoals* &c. of pyrogenic origin, and those substances which are formed by “carbonizing” organic substances by chemical treatment.

The main aspect of these various modes of resolution is undoubtedly the accumulation of carbon; and the conclusion is unavoidable that they are conditioned by the tendency of the carbon atoms to unite with one another, *i. e.* to form condensed molecules. This property of the element is the very basis of its special chemistry, and of the widest significance in the living world; and in this its last expression (*i. e.* *tending* to pass from the combined to the elementary condition) we see the crowning chapter of its remarkable history. In our interpretation, however, of this chapter we should guard against a spurious ideal, and ask ourselves, Are there any facts which warrant the conclusion that the elementary condition could be attained by any process of cumulative resolution of carbon compounds? and, further, Does not the mathematical analogy of series proceeding by a definite law of development (and that these bodies have been or can be developed through infinite series is an unavoidable inference) indicate its impossibility, except under the operation of a new cause?

Berthelot\*, we believe, was the first to apply this mode of reasoning to the case in question, and to regard the hydrogen and oxygen present in these pseudo-carbons as essential constituents, and the pseudo-carbons themselves, therefore, as a complex of compounds ( $C, H, O$ ) of very high molecular weight. Mills has given us a more general view of such molecular condensations in his theory of Cumulative Resolution†; but the attendant phenomena are in this group of resolutions too complex, and as yet insufficiently investigated, to allow of

\* *Ann. Chem. Phys.* [5] xvii. p. 139. † *Phil. Mag.* Suppl. June 1877.



exact representation. The ultimate solution of these problems cannot, therefore, be more than indicated; and it is thrown upon the experimentalist to supply the requisite data. It is an interesting fact that as early as 1805 Hatchett\* published the results of an investigation of the action of nitric acid upon these pseudo-carbons, in which he established, as a general property, that they are by this action converted into soluble bodies having the astringent and other characteristics of the tannins. His results are, it is true, of a somewhat empirical and qualitative order; they are nevertheless worthy of much more attention than they have received; and their recognition would have kept prominent the compound character of the pseudo-carbons. It is noteworthy that Berzelius† was sufficiently impressed with their importance to devote considerable space in his treatise to their reproduction. Modern writers, on the other hand, have ignored them, probably from a sense of their lacking theoretical coordination. Hatchett himself appears conscious of this, and also of some virtue in undertaking the investigation of these bodies—the products of the action of the acid,—from which, as he says, chemists have doubtless been deterred, or even repelled with disgust, by reason of the “proteus-like” changes which they undergo whilst under experiment.

In ignorance of his results, we were led to investigate certain of these pseudo-carbons, from the altogether different standpoint of their relationship to the carbohydrates. The black “carbonaceous” substance which we obtained‡ by the action of sulphuric acid at 70° C. upon cellulose, we found to be converted by the action of chlorine into a bright yellow chlorinated substance, soluble in alcohol, and resembling in composition and properties the product of the action of this gas upon the jute-fibre substance—the latter being an undoubtedly aromatic derivative, having many points of resemblance to tetrachloroquinone, and standing in close relationship to the natural group of astringents or tannins. It is not our intention to reproduce the long synthetical proof by which we sought to establish, from the chemical side, the developmental connexion of the tannins with the carbohydrates. Suffice it to say that the most direct point in the proof lay in the chemical characteristics of these pseudo-carbons; and from a study of these, as yet only superficial, we are impressed with the relations of both to the carbohydrates, the connexions being completed through infinite series of naturally-occurring

\* Phil. Trans. 1805.

† *Traité de Chimie* (translated from 4th German ed., by Valerius), iii. p. 218.

‡ Brit. Assoc. Reports, 1881.



substances. The subject is one that may be safely left to develop itself in the minds of all who contemplate the science in relation to plant-life, and will lead to the conviction of the indefinitely wide potentiality of cellulose.

Although the passage of cellulose into coal is an obvious fact, the processes by and through which the transformation has occurred lie outside the range of observation, and must remain therefore to that extent a matter of speculation. On the negative side, however, greater certainty is attainable; and the statements of Zirkel\* and Richters†, which formulate the older views of the composition of coal, viz. that it is a mixture of pure carbon with bituminous substances more or less, may be altogether dismissed. Balzer, we believe, was the first to combat these loose ideas; and in his excellent little treatise on the Formation of Coal‡, he advances, on the basis of a careful consideration of the origin and chemical characteristics of the coal-substance, the hypothesis that it consists of a mixture of complicated compounds, genetically if not homologously related, the most important feature of whose atomic structure is the union of the carbon atoms with one another, progressive condensation in this direction being expressed by decreasing susceptibility to the action of reagents. This treatment of the subject, however imperfect its development within the narrow limits of the treatise in question, has the merit of throwing the onus of proof of the presence of elementary carbon in coals and other pseudo-carbons upon those who have assumed it, and of opening up the question in its objectivity. We do not propose to enter into it more fully at present, than to say that we have obtained, by the action of chlorine upon a (Wigan) coal, a chlorinated derivative similar to those obtained by us from lignified fibres, and also observed that the whole coal-substance was so profoundly modified by the action of hydrochloric acid (diluted) and potassium chlorate as to be subsequently entirely soluble in alkalies. Our investigation of these points is proceeding; but even at this stage they indicate very clearly the developmental connexion of the coal with the cellulose constituents of growing plants.

We cannot, however, leave Balzer's brochure without noticing an incidental allusion§ to the reducing-action of the pseudo-carbons, notably charcoal, upon sulphuric acid, in which he states, as a well-received fact, that the reducing-agents are the compound constituents of the pseudo-carbons, and not elementary carbon. We have made a number of experiments upon all the pseudo-carbons, both in their normal

\* *Petrographie*, i. p. 361.

† *Chem. Centr.* 1870, p. 245.

‡ *Vierteljahrss. Zürch. naturf. Ges.* xvii. H. 1 (1872).

§ Page 15.

state and after ignition in chlorine gas; and we found that the amount of sulphurous acid formed was inversely as the percentage of carbon, those which had been ignited in chlorine exerting no reducing-action whatever. We have not been able to find that this fact is at all generally recognized; and therefore we do not think it superfluous to state it here, especially as it is an important criterion of the position of any pseudo-carbon in the series.

There is yet one other important bearing of these views which remains to be stated; and that is, their relation to the Chemical Theory of Gunpowder. If from the analysis of a normal ordnance gunpowder\* the atomic ratios of the constituents, including the hydrogen and oxygen present in the charcoal, be calculated, we obtain the following numbers:—

Pseudo-Carbon.				
KNO <sub>3</sub>	S	C	H	O
13	7	16	7	2

(excluding ash and water).

Any chemical theory of gunpowder which fails to give an account of the H and O, existing, as they do, in such important (molecular) quantity, is necessarily incomplete. Those who are, by their special circumstances and experience, in a position to investigate this point, should certainly measure the influence of the hydrogen, and the compounds of which it is a constituent, upon the properties of gunpowder. What, as an extreme case, would be the behaviour of a powder made from charcoal after ignition in chlorine? Is it not at least certain that the character of a gunpowder would be influenced by the chemical constitution of its "carbonaceous" constituents?

On the more practical side, have we any certainty that the pseudo-carbons used in the manufacture of gunpowder are those best adapted to the purpose? This is surely a matter that should not be allowed to rest on an empirical basis; and we are not aware that it has received a thorough scientific treatment. We refrain from further discussion at the present time of this and cognate subjects: we shall have achieved our object if the term proposed by us as alone applicable to the substances of which we have treated recommend itself to the judgment of chemists, and still more if the recognition which it contains of their distinctly non-elementary character prove an aid to classification.

\* Karolyi, *Phil. Mag.* October 1863.

XXXIX. *On the Constitution of the Lines forming the Low-Temperature Spectrum of Oxygen.* By PIAZZI SMYTH, *Astronomer Royal for Scotland*.\*

I HAD added (at p. 140 of my paper on "Gaseous Spectra") to the "small dispersion" account therein given of the above-mentioned spectrum of luminous oxygen gas, that two, if not four, of its very few and scanty lines appeared, when viewed with much higher dispersion, to be double, but that I hoped to give a more exact account of them, after completing some arrangements then in progress for increasing both the dispersion and magnifying-power of my spectroscope.

These improvements, together with a great advance in definition, were finished last November; and almost the first result they yielded was, to much more than confirm what I had only suspected before, and to do so, moreover, with such vigour and certainty as to make me inquire right and left for several weeks, to ascertain if what I then saw was really a new discovery, or had perhaps been known long before to older and better spectroscopists.

So far as I have been able to gather, the thing is new, and promises to be important to theorists in molecular vibrations, on account of what it fulfils. To explain this, let me refer to Dr. Arthur Schuster's valuable paper in the Transactions of the Royal Society, London, for 1879, "On the Spectra of the Metalloids: Spectrum of Oxygen." Beginning his exposition of the low-temperature spectrum (after having treated very fully of the exceedingly different high-temperature spectrum) of oxygen with the late Prof. Plücker's account of it, and concluding with his own confirmatory observations, Dr. Schuster shows that the low spectrum had always been found to consist of only four, single, wide-apart lines—viz. one in the orange, one in the citron, another in the green, and another still in the indigo-violet; and to that spectrum, containing only four such solitary, single, simple lines, the learned Doctor gave the second or *alias* name of the "compound-line" spectrum of oxygen.

The reason for such an apparent misnomer, or *lucus à non lucendo*, was, that at the very moderate temperature of electric illumination at which this trifling-lined spectrum of oxygen appears, most other gases do give forth very compound-line spectra indeed—spectra with hundreds or even thousands of

\* From the Transactions of the Royal Society of Edinburgh, vol. xxx. part 1. Communicated by the Author.

lines, arranged in peculiar bands or parcels, and known generally as fluted spectra. Hence Dr. Schuster's name for what he saw in oxygen, while principally intended to show the physical circumstances under (or temperature-level on) which it is produced, might perhaps privately have been intended to indicate that he had somehow an idea that if the lines were not compound they ought to have been, and would one day be found so to be.

That, so far as I can ascertain, is the furthest point the subject has even yet reached elsewhere; and it was at that point that I had taken it up in 1879 and 1880, in the paper already printed by this Society. In the regular course of that paper, going through many gases, with single-prism power only, I abundantly confirmed Messrs. Plücker's and Schuster's four wide-apart lines, as constituting in themselves alone almost the whole and entire low-temperature spectrum of oxygen. I did, indeed, also find a strong line in the scarlet-red, besides two in the red or ultra-red, and two in the citron-green, of extreme faintness, and only probably belonging to the same spectrum. But they did not in any way alter the apparent anomaly of the Doctor's name; for each of these new lines was also solitary: and what are after all nine, or, to keep within more certain bounds, five, simple lines standing separate and along a length where 10,000 such could take their places without interfering with each other?

But when I looked last November with the improved apparatus, what a change was there! for of the five certain lines no less than four were found to be triple, after a fluted fashion too. These four truly compound lines then were—mine in the scarlet-red, and Plücker and Schuster's three lines in the orange, the citron, and green respectively; but their last line in the indigo-violet remained persistently and positively single. Still, with four fifths of this most scanty spectrum now proved to consist of triplets instead of single lines, Dr. Schuster's original and really most happy name for it, of "the compound-line spectrum" of oxygen, was fully justified, at the same time that the miniature scale of the triplets seemed to make the physical nature of oxygen more markedly different than ever from all other known gases; for they, at the same temperature-level, generally make their bands or compound-line arrangements on a comparatively enormous scale, and in multitudinous groupings.

To those who are engaged in chemical spectroscopy it will at once convey an idea of the small-sized triplicity of these oxygen lines, to be told that from the first to the second of each triplet the distance is one fifth that of the well-known salt-line double; and from the second to the third is between

one eighth and one ninth of the same space; while the salt-line double itself is only one eighth of the average distance apart of the stronger flutings of the citron-band of the carbon-hydrogen blowpipe-flame, which band has some six or seven of such flutings within its easily perceivable breadth.

Or, again, if we should on the black board represent the separation of the first and second of any oxygen triplet by a tenth of an inch, and from the second to the third by six hundredths of an inch (when it will require a good eye from the other side of the table to separate them), that would indicate a scale for the whole spectrum, or from red to violet, of 25 feet; and that is rather more than three times as long as the late Professor Ångström's grand and almost universally followed "Normal Solar Spectrum."

For bright-line chemical spectroscopy, and especially with the faint light of incandescent gas in a low-temperature electric spark, it is by no means usual or easy to separate lines so very close together as the members of one of the oxygen triplets. A few words of explanation may therefore be demanded of me in proof that the resolution was real and not an optical deception. The propriety of the demand, too, I am quite ready to allow, knowing only too well that there are prisms which will fringe every bright line with diffraction repetitions, or, when out of the best focus, will double or treble any line, and others, again, that make them so broad and hazy that clear separation of very close lines would be utterly impossible.

As my gas-vacuum-tube spectroscope admits only of a deviation range up to  $45^\circ$ , or that of a single white-flint prism of  $52^\circ$  refracting angle, I was compelled to have recourse to compound prisms to get up the necessary dispersion for crucial cases, say that of seven or eight such prisms. Now, although some beautiful compounds were made for me both in France and this country, they invariably failed in the item of perfect definition. I then tried a large fluid bisulphide-of-carbon prism made in Paris, but failed in several ways. So lately I entered into a contract with an exceedingly skilful as well as persevering optician in London, viz. Mr. Adam Hilger, to make two large bisulphide prisms, having a clear circular aperture of 2.1 inches diameter, a refracting angle of  $104^\circ$ , anti-prisms of crown glass square at the ends, and a central angular bored block of the same material to hold the fluid.

The troubles poor Mr. Hilger had to go through were almost overwhelming. He bored through block after block of crown glass, only to find after an hour, or a day, or a week



that it fell in pieces of its own accord, until he had a heap of tunnelled fragments large enough to make a cautionary photograph of. And when he had at last succeeded by his unconquerable perseverance in securing two blocks that stood, and the anti-prisms were to be fastened on their faces, he tried almost every patented and unpatented cement before he found one, or rather a particular method of using it, which could withstand the action of the bisulphide for more than a day or two.

At last, however, though long after the contracted time, he brought the two prisms here complete; and they passed successfully through the severest trial I had prepared for them, viz. that when a hydrogen-line was at its brightest, shining like a ray of sunlight in a dark field, its light must be entirely and sharply confined to the width of opening of the slit for the time being. Not, however, until some months after, when the telescope power was also improved, and a new class of difficulties with the prisms had been overcome, could the desired trial on oxygen be made. Now, whereas I had, as mentioned already, on previous occasions with the best compound glass prisms I could procure, seen only an uncertain idea that some of the oxygen-lines might be double, I now saw the real triplicity of four of the lines, and measured them micrometrically with a degree of certainty and satisfaction that I had never dreamt of with the older apparatus; and this triplicity of these lines never came out more remarkably than when the singularity of really single lines, such as those of hydrogen impurities in the same gas-tube, was rendered most distinctly. I will therefore now only seek to conclude with a few words on the bearing of this tripleness of the oxygen-lines, first, on the disputed question of the existence of oxygen in the atmosphere of the sun, and, secondly, on the absence of hitherto recognized oxygen-manifestations (though oxygen is so well known to exist as a large part of the earth's atmosphere) in the telluric rays that become visible in the solar spectrum at sunrise or sunset.

#### *Oxygen in the Sun.*

For many years it was a sort of crying wonder that the spectroscope showed no traces in the sun of so necessary a gas to combustion as oxygen—the expected test being, that we should see there as dark lines all the lines which are seen bright when oxygen gas, on being rendered incandescent in a *high* electric temperature, then shows what is called its “elemental-line spectrum.” But not one of those lines could be detected by its dark counterpart in the sun. At length

Professor Henry Draper, of New York, from a series of experiments made with extraordinary skill and power, announced that oxygen appears in the solar spectrum not in its dark but in its bright lines, outshining where they come the brightness of the sun's continuous-spectrum background. Yet, though he gallantly made a voyage from New York to London especially to describe his experiments, and was honourably received and attentively heard, there are some persons there who are not convinced yet.

Now Dr. Schuster had already compared his four lines, though of the low-temperature oxygen-spectrum, with Ångström's normal solar-spectrum map, under the idea apparently that, though the solar oxygen might have been rendered incandescent in the very hottest central regions of the sun, it might have its Fraunhofer dark correspondences checked off by cooler oxygen vapour outside. But as his then knowledge of oxygen low-temperature lines made them only four single, simple, thin lines, the comparison was not attended with any very certain result; for there are so many of such lines, unclaimed for any element, strewed all along the solar spectrum. But now that I had found four out of five lines to be triplets of an accurate kind, could any thing further in the way of identification be ascertained?

In apparently the very place of the three fainter of the above-described triplets there is a close double of peculiarly thin Fraunhofer lines depicted by Professor Ångström in his normal solar-spectrum map; and in the place of the brightest of them, viz. Schuster's orange line, there is a triple\* of the same kind of *ultra* thin lines; and not one member of all those four groups has been claimed for any known element by the great Swedish physicist. Yet I am by no means satisfied that the degree of correspondence is conclusive, and can only hope that those who have the means will positively confront the new oxygen triples with the sun itself and inform us what they find.

#### *Oxygen of the Earth's Atmosphere in the Telluric Solar Spectrum.*

If the long silence of the spectroscope touching oxygen in the sun was a wonder, and perhaps something the reverse of praise to those who used the supposed all-powerful instrument,

\* That triplicity is indeed there broken in upon by a far stronger line, which Ångström traces to sodium (Na); but such cases of mere optical juxtaposition are frequent in the crowds of lines in much of the solar spectrum, without any physical connexion being supposed to be implied thereby.

what shall be said for its continued silence as to the presence of any free oxygen in the earth's atmosphere, when *some* gases that are therein do make themselves most signally conspicuous on the solar spectrum, in the shape of dark lines or bands, growing as the sun descends in altitude, until they become at last more grandly thick and black than all the truly solar markings put together?

Amongst these gigantic cases of Fraunhofer lines of some kind of telluric gaseous origin, we do indeed know, by a sort of inductive process rather than by any positive proof, that the band too hastily called "little *a*" and other bands and lines near C and near D are the spectroscopic proofs of *watery vapour*, as an invisible but potent gas in our atmosphere. But what makes the far greater A or great B and the  $\alpha$  (alpha) band, no one pretends to know.

At first sight it might well be suggested that they must be formed by one or other, or both, of the two grand constituents of the earth's atmosphere as established by the chemists, viz. oxygen and nitrogen. But there we are instantly met by Ångström's inflexible law, promulgated by him in 1853, and repeated at p. 39 of the description of his "Normal Solar Spectrum" in 1868, viz. that "a gas in the state of incandescence emits luminous rays of the same refrangibility as those which it can absorb"—or, conversely, when it acts by absorption, it produces dark in all the spectrum places where, when in a state of incandescence, it produced bright lines.

Now we know by laboratory experiments what bright lines are given out by both oxygen and nitrogen in various states of incandescence; and not one of those lines is in the place, and at the same time endowed with the physiognomy, of great A or great B, or of the  $\alpha$  (alpha) band of the sunset solar spectrum.

To get over this astonishing difficulty, Ångström—who held that all these three bands are of a similar visible constitution, viz. a thick line and then a band of thin lines stretching out towards the red end of the spectrum—suggested that they might be produced by "carbonic acid." But, over and above the difficulty that carbonic acid is an almost insensible impurity in the open air, and could hardly be expected to extinguish every sign of the existence of the atmosphere's two great constituents, we do know the spectrum given by incandescent carbonic acid in the laboratory, and it cannot claim to having a band in the place of either A or B or  $\alpha$  (alpha), besides its series being turned in the opposite direction, or every band vanishing towards the violet, in place of the red, end of the spectrum.

Evidently, then, in despair, this sorely tried and now departed philosopher of Upsala, but who is still our chief authority in this line, on page 41 of his memoir already cited, after acknowledging that he had, in another place, suggested "carbonic acid," says further, perhaps it is ozone which produces these bands. No reason is given; but the prudent caution is inserted—if there is free ozone in the earth's atmosphere. Or, again, he adds as a third supposition, perhaps they are produced by "fluorescence of oxygen," a gas which he there states gives forth "a faint phosphorescence in a Geissler gas-vacuum-tube when an electric current is caused to pass through it." But this is just as far from presenting us with the very definite lines constituting the bands of great A, great B, and  $\alpha$  (alpha) of the sunset telluric solar spectrum as before.

Now I have not, any more than all the rest of the world at this moment, any positive and proved means of raising Professor Ångström out of the difficulties he eventually sunk under. But the minute triplicity of the greater part of the low-temperature lines of the oxygen-spectrum, described in the beginning of this paper, may perhaps let in a chink of light upon the difficulty, when combined with the true constituent features of these grand telluric lines A, B, and  $\alpha$  (alpha), as set forth in my Lisbon solar spectrum, so recently honoured by the Royal Society of Edinburgh with their Makdougall-Brisbane Prize.

Ångström, observing these three bands when they were thick and clumsy at sunset, pronounced their constitution to be exactly similar in every case. I, on the contrary, observing them in a high sun, when they were divested of the rotundity of flesh, and only their thin, linear bones appeared, found the ultimate constitution of the  $\alpha$  (alpha) to be perfectly different from that of A and B; for in place of many regular and symmetrically arranged powerful lines, it was made up of little doublets and triplets of both inconceivable minuteness and very irregular occurrence (see the said Lisbon spectrum as printed in vol. xxix. of the Society's Transactions). These Lilliputian foundation-stones of the  $\alpha$  (alpha) band appeared to me at the time almost ridiculous in their smallness; but now I recognize them as having a close family resemblance to the triplicity of the low-temperature oxygen-lines which I have been trying hereinbefore to describe. They are not indeed the very same; for they are in different spectrum places; but they do give the idea (suggested also by some points in both the aurora-spectrum and cometary spectra not yet reproduced in any laboratory elec-

trical experiments) that there is a temperature-level in nature for the incandescence of gases, much lower than that of the low-temperature oxygen-spectrum of these pages. Wherefore, if we could artificially produce that kind of ultra-low-temperature illumination, electric probably, we might find that the  $\alpha$  (alpha) band in the solar sunset spectrum represented the oxygen, while the A and B bands showed us the nitrogen gas thereof—they two being the mighty gas constituents known so well to every one (*except telluric-line solar spectroscopists*) to exist in the earth's atmosphere, and in such overpowering quantity as to practically exclude every thing else except watery vapour.

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*XL. Regnault's Determination of the Specific Heat of Steam.*  
*By J. MACFARLANE GRAY\*.*

REGNAULT'S experiments on the specific heat of vapours have been interpreted by Regnault as giving results not at all in accordance with the deduction from the kinetic theory of gases, that, for matter travelling in single molecules, the product of the molecular weight by the specific heat is a constant for all substances. I have been led, by considering the order of temperature-pressures for steam, to conclude that the above deduction is true for steam; and I have no doubt, also for all matter travelling in single molecules. When, in 1880, I laid my conclusions before the Physical Society as being corroborated by Regnault's dynamical experiments, it was objected that Regnault's direct thermal experiments gave results widely different from my conclusions; and the report on my paper was that that difference proved that, in the corroborations I had pointed out, I had been led away by merely numerical coincidence.

I will now show that Regnault's thermal experiments have been misinterpreted by Regnault himself, and that he ought to have read the specific heat of steam, according to his experiments, to be exactly in accordance with the deduction of the kinetic theory.

The method of the experiments was to generate steam at  $100^{\circ}\text{C}.$ , to superheat it under atmospheric pressure to (say)  $125^{\circ}$  in one set of experiments, condensing it in a calorimeter to ascertain what quantity of heat was given up, down to  $0^{\circ}$ . In a second set of experiments with the same apparatus, the temperature was raised to (say)  $225^{\circ}$ , while the steam was still at atmospheric pressure; this was also condensed in the

\* Communicated by the Physical Society, having been read at the Meeting on February 25, 1882.



same calorimeter. It was found that the heat given up by the steam at  $225^{\circ}$  exceeded that given up by the steam at  $125^{\circ}$  by 48.051 units of heat; and, dividing by the difference of temperature (100), Regnault found 0.48051 for the specific heat of steam at constant pressure.

In these experiments the superheating to  $125^{\circ}$  was, no doubt, intended to thoroughly dry the steam, so as to get, in the quantity of heat abandoned in the first set of experiments, the entire heat of complete gasification, because, if still some moisture remained in the steam, the latent heat of evaporation of that moisture would be included in the difference-quantity supposed to be due to the specific heat of temperature-raising, and, by that amount, the result would be too high.

It appears to me that the completion of the evaporation of suspended moisture cannot be accomplished between  $100^{\circ}$  and  $125^{\circ}$ ; but it will be more likely to be carried on between  $125^{\circ}$  and  $225^{\circ}$ . Particles of liquid remain at the pressure-temperature whatever be the superheated temperature of the gas in which they are suspended. The rate of evaporation of those particles will therefore depend upon the temperature-difference; and in the lower range of temperatures but little of the moisture will be evaporated in its rapid passage through a worm heated to only  $25^{\circ}$  in excess of the pressure-temperature. In the second set of experiments the excess of temperature was  $125^{\circ}$ .

To test this, let similar experiments be made at  $100^{\circ}$ ; and if the resulting apparent specific heats between  $100^{\circ}$  and  $125^{\circ}$  are higher than those obtained by Regnault between  $125^{\circ}$  and  $225^{\circ}$ , then my argument is demolished; but if the results are smaller, then my suspicions have been justified, and a correction is required on the results as given by Regnault. Fortunately for my object, Regnault has left us (in vol. i., at page 695) the data of thirty-eight reliable experiments on the "total heat" of steam at  $100^{\circ}$  down to  $0^{\circ}$ , giving the mean = 636.70 units of heat. I have, with this "total heat" for  $100^{\circ}$ , compared the results of the experiments on the steam of  $125^{\circ}$ —in precisely the same way as Regnault worked for the interval between  $125^{\circ}$  and  $225^{\circ}$  (these experiments are recorded in vol. ii., pages 167–178). The results of my calculations are given below. The first two series were merely preparatory trials to arrive at the best form of apparatus; and only a few grammes of vapour were passed through the worm at each of those experiments. In the third and the fourth series ten times as much vapour was passed through on each occasion. Regnault says:—"J'ai pu opérer ainsi sur des quantités de vapeur beaucoup plus considérables, et diminuer l'importance

relative des corrections produites par les causes perturbatrices." This consideration is still more important when the range of temperature is limited to 25°—only one fourth of the range from which Regnault deduced his result. The large calorimeter was used only in the third and fourth series.

First series.	Second series.	Third series.	Fourth series.
·280	·546	·299	·386
·465	·591	·314	·381
·417	·567	·340	·346
·377	—	·375	·309
·463	Mean ·567	·400	·427
—		·411	·463
Mean ·400		·349	—
		·413	Mean ·3853
Preparatory trials.		·405	
		·415	
		—	
		Mean ·3721	

That the method of calculation may be perfectly clear, I give the particulars for the first experiment in the fourth series. Superheating to 124°·81, each unit of vapour gave up 646·28 units of heat down to 0°. Steam at 100° gave up 636·70 down to 0°.

$$\frac{646.28 - 636.70}{124.81 - 100} = .386.$$

The quantity of vapour in this experiment was 102·62 grms.; the quantity in the first of the first series was only 8·957 grms.

The fourth series was made with an apparatus which was an improvement on that used in the third series; and, taking that series only, adding the probable amount of moisture which would remain at 100° temperature (say 1 per cent. on the ·385), the result is ·389; this, on other grounds, I believe to be nearly correct. If, however, neglecting the other grounds for my opinion, we take the mean of the means of the third and the fourth series, we get

$$\frac{.3721 + .3853}{2} = .3787.$$

This is what Regnault might fairly have done.

If we now calculate what Regnault's experiments would give as the kinetic-theory result,—we get the specific heat of hydrogen, at page 121, "mean = 3·4090;" and taking the molecular weight of steam = 17·96, we find the specific heat

of steam

$$3.409 \times \frac{2}{17.96} = .3796.$$

That is to say, the kinetic theory and the thermal determination give almost identically the same number.

This is, I believe, the first experimental proof that the law of "inversely as the molecular weights" applies to compound gases.

XLI. *Acoustical Observations*.—IV. *By* LORD RAYLEIGH, *F.R.S., Professor of Experimental Physics in the University of Cambridge*.\*

On the Pitch of Organ-pipes.—Slow *versus* quick Beats for comparison of Frequencies of Vibration.—Estimation of the Direction of Sounds with one ear.—A Telephone-experiment.—Very high Notes.—Rapid Fatigue of the Ear.—Sensitive Flames.

*On the Pitch of Organ-pipes.*

IN the Philosophical Magazine for June 1877 I described some observations which proved that the note of an open organ-pipe, when blown in the normal manner, was *higher* in pitch than the natural note of the pipe considered as a resonator. The note of maximum resonance was determined by putting the ear into communication with the interior of the pipe, and estimating the intensity of sounds of varying pitch produced externally.

A more accurate result may be obtained with the method used by Blaikley†, in which the external sound remains constant and the adjustment is effected by tuning the resonator to it. About two inches were cut off the upper end of a two-foot metal organ-pipe, and replaced by an adjustable paper slider. At a moderate distance from the lower end of the pipe a tuning-fork was mounted, and was maintained in regular vibration by the attraction of an electromagnet situated on the further side, into which intermittent currents from an interrupter were passed. Neither the fork nor the magnet were near enough to the end of the pipe to produce any sensible obstruction. By comparison with a standard, the pitch of the fork thus vibrating was found to be 255 of König's scale. The resonance of the pipe was observed from a position not far from the upper end, where but little of the sound of the fork could be heard independently; and the

\* Communicated by the Author.

† Phil. Mag. May 1879.

paper slider was adjusted to the position of maximum effect. This observation was repeated many times, the distance between marks fixed on the pipe and on the slider respectively being recorded. The following numbers give the results, expressed in fiftieths of an inch:—

31	33	30	25	31
25	32	31	34	29
35	28	29	30	

The extreme range being only one fifth of an inch, shows that the observation is capable of considerable precision, corresponding as it does to only about 2 vibrations per second out of a total of 255. Finally, the slider was fixed at the mean of the above-determined positions, and the natural note of the pipe was then considered to be 255. The error in length was probably less than  $\frac{1}{10}$  inch, and the error in pitch less than half a vibration per second.

The pipe was then blown from a well-regulated bellows; and the beats were counted between its note and that of the standard fork above referred to, the pressure being taken simultaneously with a water-manometer. Three observers were found to be necessary for accurate working—one to count the beats, rising to the rate of ten per second, one to keep the bellows uniformly supplied with wind, and one to observe the manometer. At pressures between 4.2 inches and 1.53 inch the pitch of the pipe was very well defined and considerably higher than the natural note. Below 1 inch the pitch became somewhat unsteady, and distinct fluctuations in the frequency of the beats were perceived, while no corresponding variation of pressure could be detected. At about .8 inch the pitch of the pipe falls to unison with the natural note, and with further diminishing pressures becomes the graver of the two. Below .7 inch the unsteadiness is such as to preclude accurate estimations of pitch.

The results are embodied in the accompanying table, which shows the correspondence of pitch and pressure. Instead of the actual number of beats counted, which involves a reference to the extraneous element of the pitch of the standard fork, the number (greater by unity) is given which expresses the excess in the frequency of vibration of the actual over that of the natural note of the pipe. It will be seen that at practical pressures the pitch is raised by the action of the wind, but that this rule is not universal.

Pressure, in inches.	Difference of frequencies.	Remarks.
4.2	+11.0	
2.72	9.3	
2.26	8.4	
1.86	7.1	
1.53	5.6	
1.32	4.2	
1.06	2.1	
.88	1.5	
.82	+ .1	
.75	- .5	
.68	1.2	
.64	2.3	
.57	3.9*	About this point a discordant high note comes in alongside of the normal note.
.53	3.7	
.48	3.1*	Here the discordant note ceases.
.46		
.40		
.39 }	- 4.0	
.38 }		
.35 }	*	*About this point the octave of the normal note is heard, after which the normal note itself disappears.
.30	—	The normal note reappears, the octave continuing.
.26	—	The octave goes, and then the normal note, after which there is silence.
.20	+	Octave comes in again, and then the normal note, at a pitch which falls from considerably above to a little below the natural pitch. At the lowest pressures the normal note is unaccompanied by the octave.
.11	-	

*Slow versus quick Beats for comparison of Frequencies of Vibration.*

Most of those who have had experience in counting beats have expressed a preference for somewhat quick beats. Perhaps the favourite rapidity has been four beats per second. There is no doubt that in the case of insufficiently sustained sounds slow beats are embarrassing. The observer gets confused between the fall of sound which is periodic and that which is due to the dying away of the component vibrations, and loses his place, as it were, in the cycle. But it is also possible, I think, to trace an impression that, independently of the risk of confusion, quick beats can be counted with greater accuracy than slow ones. It is indeed true that the number of beats in a given time, such as a minute, can be determined with greater relative accuracy when there are many than when there are few; but it is also true, as a little consideration will show, that in the comparison of frequencies we are



concerned not with the *relative*, but with the *absolute* number of beats executed in the given time. If we miscount the beats in a minute by one, it makes just the same error in the result whether the whole number of beats is 60 or 240.

When the sounds are pure tones and are well maintained, it is advisable to use beats much slower than four per second. By choosing a suitable position we may make the intensities at the ear equal; and then the phase of silence, corresponding to antagonism of equal and opposite vibrations, is extremely well marked. Taking advantage of this, we may determine slow beats with very great accuracy by observing the time which elapses between recurrences of silence. In favourable cases, the whole number of beats in the period of observation may be fixed to within one tenth or one twentieth of a single beat, a degree of accuracy which is of course out of the question when the beats are quick.

In some experiments conducted by Dr. Schuster and myself\*, to determine the absolute pitch of a König standard fork, I had occasion to observe some very slow beats. The beating sounds were of pitch 128. One of them was steady, proceeding from an electrically maintained fork; the other (from the standard fork) gradually died away. In order to be more independent of disturbing noises to which we were exposed, a resonator was used connected with the ear by an india-rubber tube. The standard fork was mounted at the end of a wooden stick, so that it might not be heated by the hand. As the vibrations became less powerful, the prongs of the fork were caused slightly to approach the mouth of the resonator, so as to maintain the equality of the two component sounds. In this way it was possible to obtain very definite silences, and to measure the interval of recurrence with accuracy. In one observation, extending over about two minutes, the beat occupied as much as twenty-four seconds, and there was no confusion. I have little doubt that even slower beats might be observed satisfactorily if both components were steadily maintained.

*Estimation of the Direction of Sounds with one ear.*

In my former experiments (Phil. Mag. June 1877) I found it difficult to obtain satisfactory observations with one ear closed, although it was not doubtful that the power of estimating directions was greatly curtailed. My desire to experiment upon an observer deaf on one side has since been gratified by the kind assistance of Mr. F. Galton. In January 1881 experiments were tried with him similar to those on normal

\* Proc. Roy. Soc. May 5, 1881, p. 137.

hearers described in my former paper. It was found that Mr. Galton made mistakes which would be impossible for normal ears, confusing the situation of voices and of clapping of hands when to his right or left, as well as when in front or behind him. Thus, when addressed loudly and at length by a little boy standing a few yards in front of him, he was under the impression that the voice was behind. In other cases, however, there seemed to be some clue, whose nature we could not detect. Bad mistakes were made; but the estimates were more often right than mere chance would explain.

After this experience it seemed unlikely that there could be any success in distinguishing whether pure tones came from right or left, and from in front or behind. The experiment was tried, however, with in the main the expected result. But when the sounds were close, there appeared to be some slight power of distinguishing right and left, which may perhaps have been due to incomplete deafness of the defective ear.

#### *A Telephone-experiment.*

In Maxwell's 'Electricity and Magnetism,' vol. ii. § 655, it is shown that a perfectly conducting sheet acts as a barrier to the magnetic force:—"If the sheet forms a closed or infinite surface, no magnetic actions which may take place on one side of the sheet will produce any magnetic effect on the other side." In practice we cannot use a sheet of perfect conductivity; but the above-described state of things may be approximated to in the case of periodic magnetic changes, if the time-constants of the sheet circuits be large in comparison with the periods of the changes.

The experiment is made by connecting up into a primary circuit a battery, a microphone-clock, and a coil of insulated wire. The secondary circuit includes a parallel coil and a telephone. Under these circumstances the hissing sound is heard almost as well as if the telephone were inserted in the primary circuit itself. But if a large and stout plate of copper be interposed between the two coils, the sound is greatly enfeebled. By a proper choice of battery and of the distance between the coils, it is not difficult so to adjust the strength that the sound is conspicuous in the one case and inaudible in the other.

#### *Very high Notes. Rapid Fatigue of the Ear.*

In former experiments with bird-calls I had often been struck with what seemed to be the capricious behaviour of these sources of sound, but had omitted to follow up the ob-

ervation. In the spring of last year the apparent caprice was traced to the ear, which very rapidly becomes deaf to sounds of high pitch and moderate intensity. A bird-call was mounted in connexion with a loaded gas-bag and a water-manometer, by which means the pressure could be maintained constant for a considerable time. When the ear is placed at a moderate distance from the instrument, a disagreeable sound is heard at first, but after a short interval, usually not exceeding three or four seconds, fades away and disappears altogether. A very short intermission suffices for at any rate a partial recovery of the power of hearing. A pretty rapid passage of the hand, screening the ear for a fraction of a second, allows the sound to be heard again. During his visit to Cambridge in March 1881, I had the pleasure of showing this experiment to Prof. Helmholtz.

The uniformity of the sound in the physical sense may be demonstrated with a sensitive flame, which remains uniformly affected so long as the pressure indicated by the manometer does not vary. The sensitive flame may also be employed to determine the wave-length of the sound, in the manner described in the *Philosophical Magazine* for March 1879, p. 154. In the case of two bird-calls blown with a pressure of about  $2\frac{1}{2}''$  of water, the wave-lengths were found to be respectively  $1''\cdot304$  and  $1''\cdot28$ . The method was found to work easily and with considerable accuracy, almost identical results being obtained from observations of the *loops*, where the flame is *most* affected, and from the *nodes*, where it is *least* affected.

By modifying the pressures with pinch-cocks, the two notes could be brought into unison. Although both bird-calls were blown from the same gas-bag, it was not possible to keep the beats slow for more than a few seconds at a time; but that period was quite sufficient for the effects of the beats to manifest themselves in a striking manner by the behaviour of the flame. In repeating these experiments, it may be necessary to bear in mind that many people cannot hear these high notes at all, even at first. With a shorter wave-length of about  $\frac{1}{2}''$ , as determined by the flame, I was myself quite unable to hear any sound from the situation of the flame. A slight hissing was perceived when the ear was brought up close to the source; but it is probable that this was not the part of the sound that agitated the flame.

#### *Sensitive Flames.*

In the chapter devoted to this subject in Tyndall's 'Sound' (third edition, p. 231) the accomplished author remarks:—"An essential condition to entire success in these experiments

disclosed itself in the following manner. I was operating on two fishtail flames, one of which jumped to a whistle while the other did not. The gas of the non-sensitive flame was turned off, additional pressure being thereby thrown upon the other flame. It flared, and its cock was turned so as to lower the flame; but it now proved non-sensitive, however close it might be brought to the point of flaring. The narrow orifice of the half-turned cock interfered with the action of the sound. When the gas was fully turned on, the flame being lowered by opening the cock of the other burner, it became again sensitive. Up to this time a great number of burners had been tried, but with many of them the action was *nil*. Acting, however, upon the hint conveyed by this observation, the cocks which fed the flames were more widely opened, and our most refractory burners thus rendered sensitive." In the abstract of a Royal-Institution lecture (Phil. Mag. Feb. 1867) a rather more definite view is expressed:—"Those who wish to repeat these experiments would do well to bear in mind, as an essential condition of complete success, that a free way should be open for the transmission of the vibrations from the flame, *backwards*, through the gas-pipe which feeds it. The orifices of the stopcocks near the flame ought to be as wide as possible."

During the preparation of some lectures on Sound in the spring of last year, it occurred to me that light would probably be thrown upon these interesting effects by introducing a manometer on a lateral branch near the flame. In the path of the gas there were inserted two stopcocks, one only a little way behind the manometer-junction, the other separated from it by a long length of india-rubber tubing. When the first cock was fully open, and the flame was brought near the flaring-point by adjustment of the distant cock, the sensitiveness to external sounds was great, and the manometer indicated a pressure of ten inches of water. But when the distant cock stood fully open and the adjustment was effected at the other, high sensitiveness could not be attained; and the reason was obvious, because the flame flared without external excitation while the pressure was still an inch short of that which had been borne without flinching in the former arrangement. On opening again the neighbouring cock to its full extent, and adjusting the distant one until the pressure at the manometer measured nine inches, the flame was found comparatively insensitive.

It appears, therefore, that the cause of the prejudicial action of partially opened stopcocks in the neighbourhood of the flame is not so much that they render the flame insensitive as that they induce premature flaring. There are two ways in

which we may suppose this to happen. It may be that, as Prof. Barrett suggests (*Phil. Mag.* April 1867), the mischief is due to the irregular flow and consequent ricochetting of the current of gas from side to side of the pipe; or, again, the cause may lie in the actual production of sonorous disturbance of the kind to which the flame is sensitive, afterwards propagated forwards to the burner along the supply-pipe acting as a speaking-tube. The latter explanation was the one that suggested itself to my mind at the time, in consequence of the observation that a hissing sound was easily audible by the ear placed close to the half-open stopcock through which gas was passing; and it was confirmed when I found that a screw pinch-cock could be used for adjustment near the flame with impunity, in which case no sound was perceptible.

Subsequently further experiments were tried with various nozzles inserted in the supply-tube. These included holes in thin metal plates and drawn-out glass tubes. Even though the rubber tubes were so bent that the streams issuing from the nozzles were directed against the sides, no sound was heard, and no loss of sensitiveness was apparent. It would seem that mere irregularity of flow produced no marked effect, and that, provided no sound attended it, the full pressure could be borne without flaring.

These observations in no way impair the value of the practical rule laid down by Tyndall. In some cases I have found a flame flare without external excitation when a neighbouring stopcock was partially closed, and in spite of the increase of pressure recover itself when the stopcock was completely opened. When the object is to investigate the conditions of flaring, the use of a manometer near the flame is decidedly to be recommended.

March 24, 1882.

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XLII. *The Effect of Temperature on the Electrical Resistance of Mixtures of Sulphur and Carbon.* By SHELFORD BIDWELL, M.A., LL.B.\*

SINCE December 1880 I have from time to time made a number of experiments with the object of ascertaining whether sulphur could, under any circumstances, be made to exhibit the remarkable property possessed by selenium, and in a smaller degree by tellurium, of having its electrical resistance diminished by the action of light.

\* Communicated by the Physical Society, having been read at the Meeting on March 25, 1882.



Amongst other things, the effect was tried of mixing it with graphite. The sulphur was heated to a temperature a little above its melting-point ( $115^{\circ}$  C.), and when quite liquid a small quantity of tolerably pure powdered plumbago was stirred into it. The liquid mixture was then poured into moulds and allowed to cool quickly. Sticks or plates were thus produced of a substance which in general appearance closely resembled crystalline selenium, its surface being dull and slate-coloured, and its fracture metallic, not unlike that of cast iron.

A short stick of this substance was fitted with platinum electrodes (platinum wires being made red hot and pressed into the two ends), and was joined up in circuit with a Leclanché cell and a reflecting galvanometer. The spot of light was brought to the zero-point at the middle of the scale by means of a magnet, and the sulphur rod exposed to the radiation of a gas-flame which was held within a few inches of it. The spot at once began to move, showing a considerable change in the resistance of the rod. The gas-flame was extinguished; and the spot slowly returned to zero. Upon examination, however, it appeared that the behaviour of this sulphur rod differed from that of crystalline selenium in two important particulars. In the first place, the change of resistance was clearly an effect not of light, but of temperature. Burning magnesium produced no greater change than the gas-flame when held at the same distance. Sunlight was found to have a powerful effect, which was scarcely diminished when the light was caused to pass through red glass; but blue glass or a cell containing water formed an effectual screen. A black hot poker, or even the warmth of the finger, caused a greater deflection than a strong light which was too far removed to heat the rod sensibly.

Now there can be little doubt that the decrease in the resistance of selenium which occurs under the influence of radiation is totally distinct from any effect produced by temperature. It is of course true that absorption of radiations is followed by a rise of temperature, particularly when such radiations belong to the red and infra-red part of the spectrum; but it is not, I think, the fact that such rise of temperature is in any way connected with the remarkable variation of resistance under the influence of light, which, owing to the invention of the photophone, has lately attracted so much attention. The electrical effects of radiation are, in this case at least, no more due to rise of temperature than are its chemical effects. The evidence in favour of this assertion seems to me to be overwhelming; and I hope to return to it

upon another occasion, with special reference to the paper in support of the opposite view read last year by Dr. Moser.

The second point in which the sulphur rod appeared to differ from selenium, was in the *direction* of the change which the radiation of the gas-flame produced, the galvanometer showing that its resistance was increased, instead of being diminished as might have been expected. Here, however, upon the supposition that the effect is due to heating, the behaviour of the sulphur is really similar to that of selenium; for my experiments (agreeing with those of Prof. Adams) show that at ordinary temperatures slight heating is always accompanied by considerably increased resistance.

After numerous trials, in order to ascertain what proportions of sulphur and graphite yielded the greatest sensitiveness to heat, it appeared that a mixture containing 20 parts by weight of sulphur to 9 of graphite was the most suitable. It was also found to be more sensitive when cooled rather quickly than when cooled slowly, though its specific resistance (which is always high) was generally lower in the latter case.

In order that the peculiar property of the substance may be exhibited in the most effective manner, it is necessary to arrange it in thin films, so that a large surface relatively to the bulk may be exposed to the action of radiation. This was at first done by spreading it as thinly and evenly as possible upon plates of mica having tinfoil electrodes at each end. An objection to this method, however, was the enormously high resistance which it involved, amounting sometimes to several hundred thousand ohms. I therefore adopted the device which I generally use in the construction of selenium cells, and which is a simple modification of a plan originally proposed by Dr. Werner Siemens.

Two wires, preferably of platinum, are wound parallel to each other, and very close together, around a slip of mica, care being taken that the wires do not touch each other at any point. A film of the melted mixture is spread evenly over one surface of the mica; and the wire electrodes are thus connected with each other through half their entire length by a series of very narrow strips of the sulphur mixture.

The resistance of a sulphur "cell" constructed in this manner was 9100 ohms at a temperature of  $14^{\circ}$  C. The cell was slowly heated in an air-bath, and the resistance measured as accurately as possible at almost every degree. The following table sufficiently indicates the rate at which the resistance increased.

Temperature.	Resistance.
14° C. ....	9,100 ohms.
19° .....	11,400 „
25° .....	13,700 „
30° .....	16,700 „
35° .....	20,600 „
40° .....	26,900 „
45° ... ..	34,000 „
50° .....	42,900 „
55° .....	57,000 „

Thus at 55° the resistance of the cell was more than six times as great as at 14°.

Upon another occasion the cell was raised to a much higher temperature. No measurements were made with the bridge, however, the cell being simply connected with a battery and a galvanometer, and the deflections noted from time to time. After passing 55°, the resistance increased with great rapidity, until at a temperature of 100° it was sensibly infinite, there being no movement of the spot of light when the circuit was opened with a key. Immediately after passing 100°, the resistance began to fall even more quickly than it had risen. The deflection at 105° was the same as that at 85°; at 110° the same as at 65°; at 114° the same as at 50°; and at 115° the same as at 35°. The spot of light now became so unsteady (probably in consequence of the melting of the cell) that it was not possible to carry the experiment further.

A mixture has also been prepared in which lampblack was used instead of graphite; but very few experiments have yet been made with it, and the results obtained have not been uniform. At ordinary temperatures it generally behaves like the graphite mixtures; but its temperature of maximum resistance is probably lower than 100°. In one case indeed, in which the proportions were 8 parts of sulphur to 1 of lampblack, the resistance was found to be greatest at 15° (530,000 ohms), any change in the temperature, whether in the direction of heat or cold, producing a decrease. But since no such effect has been produced with other specimens of the same compound, I am inclined to think that it is due to some unnoticed peculiarity in the construction of the cell.

With this single exception, every specimen of the mixtures, whether made with graphite or lampblack, has at ordinary temperatures been found to have its resistance increased by heat.

At first sight this appears to be a very paradoxical phenomenon. It is now generally admitted that the resistance of

graphite and other forms of carbon is diminished by heat; and it is also commonly believed that a rise of temperature invariably causes a decrease in the resistance of insulators such as sulphur. The compound of sulphur and carbon with which we have to do is certainly only a mechanical mixture (for no chemical combination could be formed at a temperature of  $150^{\circ}\text{C}$ ., which is never exceeded in making the preparation); yet the effect which heat produced upon it is exactly opposite to that produced upon each of its constituents.

Some experiments were made in order to determine the effect of heat upon the resistance of carbon and sulphur separately; but, although in the case of sulphur some unexpected results were obtained, nothing whatever was observed which would *per se* account for the variations of resistance in the sulphur and carbon mixtures.

I believe the true explanation to be this:—The mixture does not consist of a uniform structureless mass of sulphur having particles of carbon imbedded in and completely surrounded by it. It is in fact an aggregation of little crystals of sulphur, with carbon packed between them like mortar between bricks. The conduction thus takes place entirely through the carbon particles, which may be considered as extending in a series of chains from end to end of the mass. Under the influence of heat, both the sulphur and the carbon expand; but the expansion of the sulphur is nearly ten times as great as that of the carbon, the net result being that the carbon particles are drawn apart, and have fewer points of contact with each other. The number of complete chains is thus diminished, and the resistance of the mass consequently increased.

It is stated in Balfour Stewart's 'Treatise on Heat,' upon the authority of Kopp, that sulphur, after being heated to a certain temperature, contracts instead of expanding. This would account for the fact that, after attaining a certain temperature, the resistance of the mixture begins once more to decrease; for the carbon particles would, when the sulphur contracts, be brought together again.

Several experiments corroborate this explanation of the variation of the resistance. Thus a mixture was made containing 3 parts of shell-lac to 2 of graphite. Though the proportion of carbon was larger than in the sulphur experiments, its resistance was found, as was expected, to be infinite; for the structureless shell-lac penetrated between and completely surrounded the carbon particles. A mixture of paraffin and graphite gave the same result.

A short rod of the usual sulphur-and-graphite compound (20 parts to 9) was fitted with platinum-wire electrodes; and its

resistance in the air at  $17^{\circ}$  was found to be 3170 ohms. The rod was immersed in a beaker of turpentine at the same temperature, and its resistance almost immediately went up about 800 ohms; and in five minutes it was somewhat higher. Though this result did not at first appear to be easily intelligible, it is fully explained by supposing that the liquid penetrated between the sulphur crystals and surrounded the carbon particles. In order to increase the effect, the beaker of turpentine containing the rod was placed under the receiver of an air-pump and the air exhausted. After remaining for a quarter of an hour in a vacuum, air was admitted, and another quarter of an hour was allowed for the action of the atmospheric pressure. At the expiration of this time its resistance was found to have increased to 15,600 ohms, about five times as great as it was originally. The rod was then placed upon blotting-paper; and three days afterwards its resistance was 2970 ohms, the temperature of the air being  $16^{\circ}$ . This was 200 ohms lower than when it was first made; but the temperature was one degree lower.

Thinking that the oil of turpentine might possibly have had some action on the sulphur, I repeated the experiment with olive-oil. On first immersion, the resistance went up from 2970 to 3150 ohms, and in six minutes to 3770 ohms. It was then left in a vacuum for forty-five minutes, after which the air was admitted, though the effervescence had not even then quite ceased; and when measured, after sufficient interval to allow the oil to penetrate, its resistance had increased to 8140 ohms. The comparative smallness of the effect produced in this latter experiment was probably due to the greater viscosity of the oil.

Lastly, since the behaviour of the sulphur-and-graphite mixture under the influence of heat seemed, like that of the microphone, to depend upon the interaction of contiguous particles of carbon, it was expected that one of the sulphur-cells before described might be used as a telephone-transmitter. This, upon trial, was found to be the case. With a single Leclanché the sounds reproduced in the receiving-telephone were feeble; but well-known nursery-rhymes were easily recognized. When, however, twenty Leclanchés were used, the sounds were much louder and the articulation perfectly distinct. No experiments whatever have yet been made with the view of developing this property; and there can be little doubt that it is capable of extension. It is not impossible that a transmitter constructed upon this principle might be found to be of practical value; and it is entirely different, at least in appearance, from any thing which has been made before.



The sulphur-cell might also perhaps be used as a thermoscope, being simpler and more easy to construct than an ordinary thermopile.

It has recently been proposed to use mixtures of sulphur and graphite for making cheap resistance-boxes. It is needless to point out that the great sensitiveness of such compounds to small changes of temperature renders them very unsuitable for such a purpose.

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*XLIII. On a Separator and a Shunt for alternate Currents of High Tension. By WILLIAM SPOTTISWOODE, M.A., LL.D., D.C.L., President of the Royal Society\*.*

[Plate IX.]

IN a former communication (Phil. Mag. 1879, vol. viii. p. 390; see also Proceedings of the Royal Institution, March 1882) I described a mode of exciting an induction-coil by means of an alternate magneto-electric machine. The machine then, and at present, used for the purpose was one by De Meritens. It answers its purpose perfectly; but it is not improbable that other alternate machines might also succeed. The method offers various advantages, several of which are described in the second paper to which reference is made above; but it also presents one considerable disadvantage—namely, that the currents produced in the secondary circuit are alternate in direction as well as in time. For some purposes this is of no consequence; but for others, such as experiments with vacuum-tubes, it gives rise to inconvenience by the production of two opposite discharges of the same strength through the tube. As these succeed one another with great rapidity, both sets are visible together, and by their presence they mask the very effects which are the subject of study.

With a view to remedy this defect many contrivances were devised; and among them it is difficult to decide how much is due to my assistant, Mr. P. Ward, and how much to myself. But it is right to state that much credit is due to him for many valuable suggestions in principle, as well as for the instrumental construction.

The first object proposed was to get rid of one set of discharges, either by preventing its passage by means of resistances, or by diverting it from the tube into a different channel. The main principle of which we availed ourselves for this purpose was found in the known property of vacuum-tubes, that a discharge is more easily effected when the negative terminal

\* Communicated by the Author.

is large than when it is small. This property is doubtless well known to most persons who have experimented in this field; but I am not aware of any special experiments made for the purpose of examining the subject. De La Rue and others have noticed that with a large negative terminal the amount of surface covered by the glow depends upon the strength of the current; and Goldstein has mentioned that the dimensions of the dark space immediately round the negative terminal depend upon the size of that terminal. Pursuing the question of the connexion between facility of discharge and the size of the terminals, we found not only that the facility depended less on the relative than on the absolute magnitudes, but also that the size of the positive may be reduced indefinitely without interfering with the discharge. Indeed, when we reflect on the appearance of the discharge under ordinary circumstances, and consider that, whatever be the size or shape of the positive terminal, the discharge at that end always proceeds as from a point, then we are almost brought *à priori* to the conclusion that the positive terminal itself may be reduced to a point without affecting the discharge. The reverse, however, is the case with the negative terminal; for, without entering more deeply into the question, it is clear that, if we reduce the surface of that terminal below the extent which would have been covered by the glow when unrestricted, we thereby interfere with the natural development of the discharge. In accordance with this consideration, we found that, when one terminal was small, in that one the discharge which was positive passed freely, while the opposite discharge failed altogether to pass; and thus in this case the problem, as it were, solved itself. The same results were obtained even when one terminal was reduced to a mere point. Acting on this principle, we inserted a tube, having one very small and one large terminal, in series with the tube which was the subject of experiment; and by means of it as an auxiliary tube we succeeded in shutting off one set of currents from the main tube.

Another, although not more successful, accessory for the same purpose was found in a tube furnished with a series of diaphragms each having a small aperture, with a tubular process leading from it and coincident with the axis of the tube. This form of tube is known as a Holtz tube; and it possesses the property of allowing the passage of discharges directed towards the tubular processes, but of impeding the reverse discharges. Speaking more accurately, each of these apertures offers resistance to the passage of the electricity in either direction, but more so to that in which the end of the

tubular process is positive than to the reverse. In some cases this is sufficient to extinguish the discharge. Advantage was taken of this fact, by using a tube furnished with several diaphragms, behind each of which was a terminal which exposed a minute point of metal only. With a stronger current a greater number of diaphragms was used in circuit; with a weaker current, a smaller number; and we were thus enabled to adjust the resistance to the strength of current employed. When several diaphragms were used the resistance became very great.

The Holtz tube, although in some ways very convenient for use, is not without its drawback; for the narrow tubular processes offer some (and not inconsiderable resistance) even to the discharges which they allow to pass. This inconvenience was obviated by substituting for the Holtz tube a column of glycerine and water in which were inserted two terminals, one consisting of a fine point and the other of a plate. The rod which terminated in the point could be raised or lowered according as it was required to increase or to diminish the length of the column, and thereby the resistance employed. By mixing the water and the glycerine in various proportions, the resistance of the column could be varied within very wide limits; and by making the mixture as weak as possible compatibly with the requirements of the case, the instrument, or electrical valve as it may be termed, could be made one of extreme delicacy.

The next step consisted in turning to account the set of currents which had hitherto been merely shut off and not utilized. The arrangement whereby this was effected will be best understood by the diagram (Plate IX. fig. 1). A and B are the two terminals of the coil; C and D, two glycerine-and-water valves; E, a glycerine shunt; F and G, two tubes, or other passages for the currents. When the current, positive at A, enters C, it passes through the valve to the tube F, and thence to the opposite terminal B of the coil. When the current is negative at A, it is unable to pass through the valve C, and it is diverted to the tube G. The same current, positive at B, passes through the valve D, also to the tube G. The complete instrument may be called a separator.

Thus far we have succeeded in separating the two sets of currents, and in diverting one set, so as to make use of them in a second tube or other channel. We have in fact disentangled the two sets; but we have done this at the expence of either making use of only one set, or at best of making use of both in two separate tubes. It is, however, but seldom that more than one tube is required at the same time for experi-

mental purposes; so that, although the last-mentioned arrangement might serve for a display, it can hardly be said to give much promise of practical utility.

We next devised another plan whereby both sets of currents can be turned to account in the same tube with much advantage. If instead of two tubes we take a single tube and furnish it with two sets of terminals, then, if we connect one pair of terminals of the separator with one pair of terminals of the tube, and the other pair of the separator with the other pair of tube, in such a way that both sets of currents enter the tube at the same end, we shall have a double set of discharges in the same direction through the tube.

It was, however, further found that it was not necessary to have four terminals in the tube; for, taking advantage of the difficulty in effecting a discharge when the negative terminal is small, we fixed two very small terminals near one end of the tube and one large one at the other. We then connected the two small terminals directly with the two sides of the machine respectively (that is, before the currents entered the separator), and the one large terminal with the two sides of the machine after the currents had been led through the two branches of the separator respectively. This effected the object desired; for, in the first place, there was no tendency in the discharge to pass from one small terminal to the other on account of the principle above quoted; secondly, there was no tendency in the current to become short-circuited at the single large terminal, on account of the difficulty in the passage of the current backward through either branch of the separator. Consequently every current issuing from the machine was obliged to pass to one or other of the small terminals, and thence through the tube to the large terminal at the other end. The scheme of the connexions to the various parts of the apparatus will, however, be best understood by reference to the diagram (Plate IX. fig. 2).

The arrangement may therefore be said to have completely solved the problem of producing unidirectional discharges through a tube from an alternating machine, and at the same time utilizing all the currents from the machine. The method has also the advantage of making the number of currents discharged through the tube in a given time double that which would have been discharged if one set of currents had been merely diverted as in the arrangement first described.

But beside shunting off, or diverting, one set of currents, it was often desirable to reduce the strength of the whole to suit the condition of the tube or the circumstances of the experiment. The readiest method of effecting this appeared to be

to introduce a resistance in the primary circuit. But this proved to be wanting in the delicacy required; and it was found necessary to operate directly on the secondary. Mr. De La Rue had, it is true, already constructed a platinum-wire resistance of 1,000,000 ohms; but even this amount was insufficient for our present purposes, while its cost was almost prohibitory. Columns of acidulated water proved very effective; but they were open to the objections, first, of heating during use, and, secondly, of evaporation of the water at all times. Both of these actions tended to diminish the resistance of the column.

Mr. De La Rue had also constructed a resistance, consisting of a thin film of plumbago spread upon ebonite; but the current heated the plumbago to such an extent that the ebonite was burnt. The instrument in question was therefore never used. Mr. Ward suggested the employment of slate instead of ebonite; and accordingly he constructed the instrument actually in use, and represented in fig. 2. The slab of slate is about two feet in length and two inches in breadth. It is fixed at an angle of about  $30^\circ$  to the horizon, the inclination being so adjusted that a block of lead, which serves as a contact piece, will slide freely down the inclined plane. A fine wire attached to the block, and passing over a pulley at the upper end, regulates the length of the plumbago actually in circuit. It is found most convenient to use this instrument (which proves to be one of great delicacy) as a shunt.

A more convenient form of this instrument consists of a vertical rod of ground glass, porcelain, or other incombustible nonconductor, having its surface slightly roughened so as to hold the plumbago. One terminal consists of a double slider capable of being elevated or depressed, and making good contact, either by a spring or by gravity, with the plumbago film.

#### XLIV. *Note on Transformation.*

By Sir JAMES COCKLE, M.A., F.R.S., F.R.A.S., &c.\*

54. **I**N my recent papers (see the Numbers for September 1881 and for January last) the details of calculation are kept within narrow limits. There are, however, various independent sources of verification, viz. substitution, reducibility of radicals, comparison of formulæ with other results and with each other, and, finally, an actual transformation.

55. In art. 2 put  $e=a$ ; the formulæ of arts. 8, 9 hold for all values of  $n$ . Put  $a, f, h=e, g, k$ ; the like is true, and the

\* Communicated by the Author.



transformed equation is free from  $x^n$ . Put  $a, e=1$  and  $h, k=0$ ; the factors are in arithmetical progression, as, by art. 13, they should be. Put  $A, E=1, 2$ ; then art. 19 gives

$$P_2=0, \quad Q_2=4+9M-12L, \quad R_2=32+18N-3M, \\ S_2=6N+12.$$

Hence

$$2B_2=16+12(L-M+N)=16+12b,$$

and

$$6C_2=12L-6M \text{ or } C_2=b+L-N;$$

and the first two conditions of art. 20 are satisfied, as is the last; for, by art. 18,  $b_2=b+2$ .

56. Since  $\eta$  and  $\eta_2$  are to be taken as one-valued when the quantities in terms of which they are expressed are so taken, we infer that the radical in arts. 10 and 17 means the appropriate root, not either root indifferently, and that the root can be rationally expressed. This is the case; irrationality has disappeared from all our results.

57. Multiply the products  $\alpha_1\alpha_2$  and  $\beta_1\beta_2$ , wherein the factors are in order of magnitude, into  $\gamma$ . If we preserve the order, we get six configurations, viz.  $\gamma\alpha_1\alpha_2$ ,  $\alpha_1\gamma\alpha_2$ ,  $\alpha_1\alpha_2\gamma$ , and  $\gamma\beta_1\beta_2$ ,  $\beta_1\gamma\beta_2$ ,  $\beta_1\beta_2\gamma$ . Assume that there is a value of  $\gamma$  which will make one of the  $\alpha$  set and also one of the  $\beta$  set an arithmetical progression. We get nine mutually exclusive but severally possible pairs of relations, of which one, for example, is

$$\alpha_2+\gamma=2\alpha_1, \quad \beta_2+\gamma=2\beta_1;$$

whence

$$4\alpha_1-2\alpha_2=4\beta_1-2\beta_2 \text{ or } 3I=3J+U. \quad \dots (14)$$

Let  $\alpha$  be taken to represent  $D-\alpha$ , and we thus obtain by Boole's algorithm a result included in those of art. 50. The same thing holds for the remaining eight cases.

58. This last verification indicates that a factor always disappears from (13), and that the solution  $\eta_2=-1$  must be expunged from art. 53; for, by art. 36,  $\omega=0$ . In the numerator of (13) of art. 50 change  $D$  into  $D-3$ , or, rather, omit the transformation by which  $D$  has replaced the  $D-3$  which would otherwise have remained there. A factor will disappear if any one of the nine expressions  $4\omega \pm 3(J \pm I)$ ,  $4\omega \pm 3I$ ,  $4\omega \pm 3J$ ,  $\omega$  vanishes. But these conditions coincide with those of arts. 33, 34, and with those implied in art. 57.

59. The introduction of the arithmetical progression, while it affords a good verification, restricts generality. Putting

$$B=A-\frac{1}{2}, \quad \Delta=D+a_2-1, \quad z=x^{a_2}X^{-\frac{\eta_2}{3}}\zeta, \\ f(\Delta, B, I)=(\Delta+2B)(\Delta-B+\frac{3}{4}I)(\Delta-B-\frac{3}{4}I),$$

I find that the binomial terordinal deducible from that in  $z$  (arts. 16, 17) is

$$f(\Delta, B, I)\zeta + f(\Delta + 2\omega, B - \omega, J)x^3\zeta = 0, \quad . \quad . \quad (15)$$

from which a factor, viz.  $\Delta + 2B$ , may be made to disappear.

60. Getting rid of this factor, putting  $Z = x^{-B}\zeta$ , and  $a_2$  (which is arbitrary) = 1, and changing  $x^3$  into  $x^2$ , we are led to

$$(D + \frac{1}{2}I)(D - \frac{1}{2}I)Z + (D + 2\omega + \frac{1}{2}J)(D + 2\omega - \frac{1}{2}J)x^2Z = 0.$$

61. But, the restriction entailed by the progression being removed, we can employ both the values of  $\omega$  given in art. 42, and so obtain two equations either of which is a transformation of the other.

62. In verification I add that, by a further application of Boole's process, these two equations may be put under the respective forms

$$(D - \beta_1)(D - \beta_2)u + (D - \alpha_1)(D - \alpha_2)x^2u = 0,$$

$$(D - \beta_1)(D - \beta_2)u_2 + (D + U - \alpha_1 - 2)(D + U - \alpha_2 - 2)x^2u_2 = 0,$$

and that one of these forms is a transformation of the other, viz.  $u_2 = (1 + x^2)^{1 - \frac{U}{2}}u$ .

63. If in  $b_2 = -\eta_2(\eta_2 + 3)$  we for  $\eta_2$  substitute  $3 - b_2^{-1}B_2$  and reduce, we get

$$b\{b + 3\omega(\omega + 1)\}\{b + 3(\omega + 2)(\omega + 3)\} = 0; \quad . \quad . \quad (16)$$

and from  $(N_2 - L_2)^{-1}(C_2 + b_2) = 3 - b_2^{-1}B_2$  we get

$$\{b + 3\omega(\omega + 1)\}\{b(\Omega - 1) + (\omega + 3)(N - L)\} = 0. \quad . \quad (17)$$

64. Both (16) and (17) are satisfied if  $b + 3\omega(\omega + 1) = 0$ . This is the solution which I have discussed. They are also both satisfied if  $b = 0$  and  $\omega + 3 = 0$ . This solution is inadmissible; for it would make  $\eta_2$  a vanishing fraction. There remains the system

$$\left. \begin{aligned} b + 3(\omega + 2)(\omega + 3) &= 0, \\ b(\Omega - 1) + (\omega + 3)(N - L) &= 0; \end{aligned} \right\} \quad . \quad . \quad (18)$$

which is important, but which I shall not discuss in these pages. The latter solution of art. 26 is not irrelevant to the system (18).

2 Sandringham Gardens, Ealing,  
March 14, 1882.

#### Erratum.

Vol. XII. p. 196, art. 36, lines 10, 11, transpose "one is" and "two are" and in line 12 *dele* integers.

XLV. *On the Fluid Density of certain Metals.* By W. CHANDLER ROBERTS, F.R.S. and T. WRIGHTSON, Memb. Inst. C.E.\*

[Plate VII.]

AT a Meeting of the Physical Society, on February 12, 1881†, we communicated the results of certain experiments, made with the aid of the oncosimeter, on the fluid density of bismuth, in which we showed that the densities in the fluid and cold solid states are respectively 10·055 and 9·82, the fluid density thus being 2·4 per cent. higher than the cold solid. These determinations correspond closely with results that had been obtained by one of us, using the “cone” method devised by Mr. Mallet‡. For the sake of convenience we here reproduce our results on bismuth.

No. of expt.	Diameter of ball, in inches.	Weight, in troy ounces, including the stem for attachment.	Specific gravity of cold ball, including the stem.	Floating effect on first immersion, in troy ounces.	Deducted specific gravity of fluid metal.	Remarks.
31.	2	23.33	9.72	1.0	10.13	Bismuth ball in fluid bismuth. Iron ball in fluid bismuth. Bismuth ball in fluid bismuth.
32.	2.25	22.184	6.99 (iron)	9.3	9.92	
33.	do.	33.46	9.755	1.3	10.11	
34.	do.	33.37	9.757	.6	9.94	do.
35.	do.	33.53	9.774	.7	9.98	do.
36.	do.	22.184	7.02 (iron)	10.2	10.25	Iron ball in fluid bismuth.
Mean ..... 10.055						
Specific gravity of solid bismuth ..... 9.82						

Since these results were published we have extended the experiments to the following metals—copper, lead, tin, zinc, silver. The results are now submitted to the Society.

\* Communicated by the Physical Society, having been read January 28, 1882.

† Proc. Phys. Soc. vol. iv. p. 195; and Phil. Mag. [5] vol. xi. 1881, p. 295.

‡ Proc. Roy. Soc. vol. xxii. p. 366, and vol. xxiii. p. 209.

*Copper.*

Six experiments were made with the oncosimeter\* on copper; four of these were made with cast copper balls  $2\frac{1}{4}$ " diameter, one with a cast-iron turned ball  $2\frac{1}{4}$ " in diameter, and one with a copper ball 3" in diameter. The first four were made with a spring that lengthened  $\frac{1}{4}$  inch per ounce troy; the last two with a more sensitive spring, giving  $\frac{1}{2}$  inch elongation per ounce troy. It will be seen by the accompanying table that the fluid density does not vary much, although, as has just been stated, the conditions were varied.

No. of expt.	Diameter of ball, in inches.	Weight, in troy ounces, including the stem for attachment.	Specific gravity of cold ball, including the stem.	Sinking effect on first immersion, in troy ounces.	Deducted specific gravity of fluid metal.	Remarks.
37.	2.25	26.357	8.23	nil.	8.23	Copper ball in fluid copper.
38.	do.	27.005	8.463	.2	8.4	
39.	do.	26.25	8.288	.5	8.13	
40.	do.	25.923	8.281	.2	8.217	
41.	do.	22.186	7.02 (iron)	Floating effect 3.5	8.127	Iron ball in fluid copper.
42.	3	64.237	8.61	Sinking effect 3.0	8.2	
Mean ..... 8.217						
Specific gravity of solid copper ..... 8.8						

The mean of these results gives 8.217 as the density of fluid copper. This metal melts at a temperature which exceeds  $1000^{\circ}$  C., and, when melted in air, absorbs oxygen. We found, for this reason, that it was not possible to obtain trustworthy results by Mallet's method, even though the cone was filled with an atmosphere of coal-gas.

\* A description of this instrument was published in the Journal of the Iron and Steel Institute, part 2, 1879, p. 418.

*Lead.*

Three experiments were made with the oncosimeter, the results being as follows:—

No. of expt.	Diameter of ball, in inches.	Weight, in troy ounces, including the stem for attachment.	Specific gravity of cold ball, including the stem.	Sinking effect on first immersion, in troy ounces.	Deducted specific gravity of fluid metal.	Remarks.
43.	3	83.37	10.7	3.5	10.25	{ Lead ball in fluid lead. do. do. Fluid lead getting cold.
44.	3	83.8	10.8	3.25	10.38	
45.	3	84.01	11.07	3.7	10.5	
Mean ..... 10.37						
Specific gravity of solid lead ..... 11.4						

A mean of two experiments on lead, made on Mallet's system, gave 10.65 as the liquid density, the results being 10.63 and 10.66 respectively.

The diagram No. 1 (Plate VII.), gives the results of the experiments on lead; and the calculations of fluid density are in each case attached, the point *a* indicating in each the position taken as giving the true initial sinking effect at the moment of immersion.

*Tin.*

Two experiments were made with the oncosimeter, with the following results:—

No. of expt.	Diameter of ball, in inches.	Weight, in troy ounces, including the stem for attachment.	Specific gravity of cold ball, including the stem.	Sinking effect on first immersion, in troy ounces.	Deducted specific gravity of fluid metal.	Remarks.
46.	3	55.66	7.165	1.1	7.02	{ Tin ball in fluid tin.
47.	Failure.					
48.	3	55.66	7.185	1.2	7.03	do.
Mean ..... 7.025						
Specific gravity of solid tin ..... 7.5						



The diagram No. 2 is reduced from the oncosimeter diagram, experiment 48.

A mean of three experiments on tin, made on Mallet's method, gave 6·974 as the liquid density—the results being 6·903, 6·982, and 6·976 respectively.

*Zinc.*

Three experiments were made with the oncosimeter on this metal, the results being tabulated below:—

No. of expt.	Diameter of ball, in inches.	Weight, in troy ounces, including the stem for attachment.	Specific gravity of cold ball, including the stem.	Sinking effect on first immersion, in troy ounces.	Deducted specific gravity of fluid [metal.	Remarks.
49.	3	52·52	6·893	2·4	6·57	{ Zinc ball in fluid zinc.
50.	3	52·58	6·901	3·3	6·47	
51.	3	52·32	6·903	3·75	6·4	
Mean ..... 6·48						
Specific gravity of solid zinc 6·8 to 7·2 (Rankine).						

The crucible was kept in the furnace during the three experiments, and maintained as nearly as possible at the same temperature throughout.

Only one determination of this metal has been made by Mallet's method, giving a liquid density of 6·55.

*Silver.*

We looked with much interest to the experiments on the density of molten silver for several reasons—mainly from the fact that it melts at a high temperature, which has been determined with great care by the late Henri Ste Claire Deville, who in his later experiments on the subject fixed the temperature at 940° C.\* We operated on a thousand ounces of silver, which proved on assay to contain 998 parts of pure silver in 1000. We have as yet only secured one trustworthy result, as we found it very difficult so to adjust the temperature of the molten silver as to prevent the silver balls from melting either too rapidly or too slowly. In the experiment No. 52, in which we did secure a result, the metal must have been just about its melting-point, as at the end of four

\* *Comptes Rendus*, t. xc. (1880) p. 773.

minutes the silver ball had not entirely melted; the experiment was stopped, however, as the silver began to solidify on the iron stem of the ball.

The diagram No. 3 is reduced from the original; and we have appended the calculation for fluid density, assuming the position of equilibrium at first immersion of the ball to be at point *a*.

The particulars of the experiment are as follows:—

No. of expt.	Diameter of ball, in inches.	Weight, in troy ounces, including the stem for attachment.	Specific gravity of cold ball, including the stem.	Sinking effect on first immersion, in troy ounces.	Deducted specific gravity of fluid metal.	Remarks.
52.	3	74.8	10.068	4.1	9.51	{ Pure silver ball in pure silver.

The liquid density of pure silver, as determined by one of us\*, on Mallet's method, from a mean of two experiments, giving respectively 9.447 and 9.476, was 9.46. This confirms the single result obtained by the oncosimeter.

If we now tabulate the mean results of the foregoing experiments, as well as those previously obtained, we shall be able to compare the densities according to the two methods of investigation:—

Fluid density of	By Mallet's method.	By oncosimeter.
Bismuth .....	10.039	10.055
Copper .....	.....	8.217
Lead .....	10.65	10.37
Tin.....	6.974	7.025
Zinc .....	6.55	6.48
Silver.....	9.46	9.51

The difficulties connected with the working of the oncosimeter are less than those which arise in Mallet's method; and the sources of error are less, the correctness of the result in the latter depending on the metal in the cone being free from air-holes.

It will be seen from the above table that, in the case of

\* Roberts, Proc. Roy. Soc. vol. xxiii. p. 493.

the five metals in which both systems were tried, the results correspond as closely as could be expected, taking into consideration the great difficulties of observation at the high temperatures employed. We therefore venture to think that the oncosimeter can be depended upon generally for the determination of the fluid densities of metals, if the experiments are conducted with the necessary care.

Taking therefore the oncosimeter-results as approximately accurate, we find the change of volume of these metals in passing from the cold solid to the liquid state to be as follows:—

Metal.	Specific gravity of solid.	Specific gravity of liquid.	Percentage of change in volume from cold solid to liquid.
Bismuth .....	9.82	10.055	Decrease of vol. 2.3
Copper .....	8.8	8.217	Increase of vol. 7.1
Lead .....	11.4	10.37	do. do. 9.93
Tin .....	7.5	7.025	do. do. 6.76
Zinc .....	7.2	6.48	do. do. 11.1
Silver .....	10.57	9.51	do. do. 11.2
*Iron (No. 4, foundry, Cleveland) .....	6.95	6.88	do. do. 1.02

The experiments just described lead us to believe that, although the conditions under which they are made may render it impossible to obtain results that are rigidly accurate, still the errors are inconsiderable. It has been urged that the unsoundness or porosity in the casting would disturb the accuracy of the results; but this is provided against in each case by taking the specific gravity of the ball operated on, its iron stem being submerged in water to a point which is afterwards just reached by the molten metal. It has also been suggested that the expansion of the ball, when it enters the fluid metal, causes tension on the metal in the interior of the ball, and that therefore the density of the ball (from which the fluid density is determined) can never be trusted. It must be remembered, however, that the determination of the fluid density is made and automatically registered at the moment of immersion, before the volume of the ball can be practically affected.

Since our last paper was read, we have seen that MM. F. Nies and A. Winkelmann† have been investigating the changes in volume of certain metals when melted. Their method will

\* Wrightson, Journal of the Iron and Steel Institute, No. 1 (1880), p. 20.

† *Sitzungsberichte der Akademie der Wissenschaften zu München*, 1881, part 1, p. 63.

be best understood by a short description of the way in which the metal tin was treated by them.

Tin was melted in a suitable vessel, the melting-point (viz.  $226^{\circ}5$  C.) being carefully maintained. Pieces of tin were then dropped in, and observed first to sink, then to rise before melting—showing that solid tin has a higher specific gravity than the liquid mass, but that when its temperature has been raised to the melting-point, or rather to a certain temperature just below, then it is specifically lighter. In order to determine this relation, they enclosed pieces of copper (having a higher specific gravity than tin) in pieces of tin, and were thus able to increase the specific gravity of the solid piece at will; and although not able to determine directly whether the compound piece was of the same density as the liquid, the latter not being transparent, yet by varying the amount of copper enclosed in the tin, thus forming pieces of a different density, they were enabled to say that it lay between the two limiting values. Compound pieces with varying and known amounts of copper, thus formed, were placed on the surface of the liquid tin for some little time, then dipped under the surface; and it was noted whether they rose again or not. The pieces were each then carefully taken out again and weighed, to ascertain that no part had been melted. This was continued until they found two compound pieces such that, at a temperature just below the melting-point, one would just rise and the other would just sink.

If, then, the relative densities of the liquid tin and the copper at the temperature of liquid tin could be ascertained by experiment, the relative density of the solid tin just below melting-point and the liquid tin can be calculated.

A copper ball was heated to the temperature of the melting tin, and weighed, first in air, then in the liquid tin. The relative densities being thus ascertained, the calculations, which we need not give here, are of a simpler character.

In the case of tin, they found that the liquid is of  $\cdot 7$  per cent. greater density than the hot solid at a temperature just below melting-point.

This, so far as it goes, is confirmatory of the results obtained by us. If diagram No 2. be examined, it will be seen that the line of volume rises gradually to the line of equilibrium, indicating expansion; and just before the ball melts rises above the line, indicating a floating effect, when the temperature approximates to the melting-point.

Tin therefore appears to be similar to iron; viz. it is at its maximum density when cold, and at its minimum density when at a temperature just below melting, and that the fluid-density is between the two.

The results obtained by MM. Nies and Winkelmann on bismuth will serve to illustrate the degree of approximation of these limiting values.

A piece of bismuth, when allied with a platinum block weighing 21·76 grammes, sank ; and another piece, weighing 35·4 grammes, floated; which is equivalent to stating that the specific gravity of the melting bismuth is between 10·28 and 10·12.

They arrive at the general result that not one of the eight metals they examined will justify the assertion that "bodies contract on becoming solid;" but the experiments rather favour the view that metals when solid, *at a temperature close upon their melting-points*, are less dense than when molten.

Without accepting MM. Nies and Winkelmann's results as final, we do not consider them to be opposed to our own, as theirs relate solely to the ratio of the densities of the solid and liquid metals at as nearly as possible the same temperature, while our experiments were undertaken with a view to determine the actual density of a metal at the *lowest* temperature at which it is perfectly liquid.

## XLVI. *Notices respecting New Books.*

*Geology of the Environs of Tokio.*

By Prof. DAVID BRAUNS, *Ph.D., M.D.* Tokio: 1881.

THE present memoir is one (No. 4) of a series published by the University of Tokio, and contains a description of the Geology of the Environs of Tokio, which are part of an extensive plain, the largest in the Japanese Empire, everywhere constructed on the same plan, and showing essentially the same formations, which consist of alluvial, diluvial, and Tertiary deposits; the bounding hills and mountains, which form a vast quadrant, are composed of Palæozoic and various crystalline rocks.

The plain or plateau of Tokio, although not much elevated, is intersected by deep cuttings of river-valleys and ravines with much alluvial matter; from which it occurs that all the diluvial parts of the plain appear as isles or peninsulas, divided from one another by those river-valleys and side valleys down to the most minute undulations of the ground. This division of the surface of the plain is of the highest importance for agriculture—the rice-fields being in most instances confined to the lower or alluvial tracts, whilst on the higher level we find the cereals, many kinds of beans, the plantations of tea, of the mulberry-tree, and most of the small forests. According to the author, this widely spread plateau must have been deposited by the sea and under its surface, and therefore must have risen above the level of the sea since the diluvial epoch in which it was formed; for it is to be noticed that in no part of it is there any trace of glacial deposits or of glacial action.



The alluvial and so-called diluvial deposits are described in the second and third chapters; in the latter, organic remains are not very numerous in the environs of Tokio; there are plant-remains of surviving species, and land, freshwater, and marine Mollusca of existing Japanese forms. The remains of mammals are rather limited: bones of Deer and Cetacea occur; also two species of Elephants, which are referred to *Elephas meridionalis* and *E. antiquus*, forms belonging to the Glacial and Preglacial fauna of Europe.

The succeeding chapters (4-7) treat of the Tertiary deposits of Oji, Tokio, Yokohama, and other parts of Japan, and of the Mollusca found in them, which are all living species; many, however, are not now found in the neighbourhood of Japan, nor even in the Pacific. In many respects, Dr. Brauns says, the Japanese shell-layers have the greatest resemblance to the *Crag*, and, next to it, to the younger Subapennine deposits, while the rocks resemble very closely the European *Faluns*.

With the memoir are given some sections and a sketch map of the environs of Tokio, and six plates of fossil shells, which are highly creditable to the Japanese artist, Mr. H. Hirauchi, who designed the illustrations.

*The Theory of Equations; with an Introduction to the Theory of Binary Algebraic Forms.* By W. S. BURNSIDE, M.A., and A. W.

PANTON, M.A. Longmans, Green, and Co.: London. Pp. 387.

STUDENTS of Mathematics are greatly indebted to the authors of this work for having combined in one volume the substance of the best standard books on the subject, with the improvements and extensions it has received at the hands of modern investigators, whose memoirs have hitherto been chiefly contributions to various Mathematical Journals. The first ten chapters comprise all the essential propositions included in the best treatises on the Theory of Equations. In the more advanced portions of the subject, Chapter XI., on Determinants, and Chapters XIV. and XV., on Covariants and Invariants, are distinguishing features of the work. To beginners these chapters are of the greatest value, not only on account of the simple and lucid manner in which they are written, but the care which has been taken to place before the student the most recent improvements in this Calculus.

The book is unusually well got up in every respect. The type, which is of various kinds, is remarkably clear: and the book altogether a triumph of the printer's art.

*Celestial Objects for Common Telescopes.* By the Rev. T. W. WEBB, M.A., F.R.A.S. Fourth Edition, 493 pp., with numerous figures. London: Longmans, Green & Co. 1881.

THIS excellent book, every page of which teems with information, is unquestionably not only the best and handiest companion for the observatory, but also for the amateur who studies astronomy for mere amusement. The questions, What is to be looked for? and How is it to be looked for? are abundantly answered in its pages.

And we know that in the compilation of the work this was the main object of its author. On opening it for the first time, the student cannot do better than turn to Appendix I. and make the corrections indicated there. Marked and important features of the manual are a map of the Moon, and a clear and not overcrowded index to it, Double Stars, Clusters, and Nebulæ, from Struve's famous 'Catalogue,' Smyth's 'Cycle of Celestial Objects,' and the more recent accurate observations of Burnham and others; while an Appendix contains the same objects placed, for the sake of convenience, in the order of their R.A.

The labour bestowed on Part III. and the Appendices must have been enormous; and great praise is due to the author for the way in which it has been accomplished. Some at least of the materials used in compilation must themselves have caused great trouble by the careful sifting they needed. Smyth's 'Cycle of Celestial Objects,' for instance, is a work not to be relied on for general accuracy.

With regard to Part II., we may note, *en passant*, what appear peculiar faults of omission and commission when we consider what a surprising amount of detail is given elsewhere. No mention is made of Mercury's distance (35,500,000 miles) from the Sun. Neither the dimensions of Venus nor her distance from the Sun are given. On page 172 a very curious and puzzling description of Saturn is given. Part of it runs thus:—"The Globe. Though about 69,200 m. in equatorial diameter, second only to Jupiter, and about nine times larger than the earth," &c. We are afraid that young students, not knowing that spheres are to one another as the cubes of their diameters, would take this sentence to mean that Saturn is only nine times the size of the Earth. The rest of the sentence is simply beyond human comprehension. However, the book amply fulfils its object, and ought to find a place wherever an astronomical telescope is in use, whatever its range may be.

## XLVII. *Proceedings of Learned Societies.*

### GEOLOGICAL SOCIETY.

[Continued from p. 147.]

January 25, 1882.—R. Etheridge, Esq., F.R.S.,  
President, in the Chair.

THE following communications were read:—

1. "On the Fossil Fish-remains from the Armagh Limestone in the Collection of the Earl of Enniskillen." By James W. Davis, Esq., F.G.S., F.L.S.

2. "On an extinct Chelonian Reptile (*Notochelys costata*, Owen) from Australia." By Prof. Owen, C.B., F.R.S., F.G.S.

3. "On the Upper Beds of the Fifeshire Coal-Measures." By the late E. W. Binney, Esq., F.R.S., F.G.S., and James W. Kirkby, Esq.

These beds are best exposed in Fife, between the mouth of the

Leven and East Wemyss. The coal-field of the latter district is the most northerly piece of true Coal-measures in Britain; they dip  $10^{\circ}$  E., or even less. The highest member (which may possibly be even later than the Carboniferous Period) is an unfossiliferous purplish sandstone, full 200 feet thick; next comes soft red marl, 12 feet, followed by sands (290 feet), marls, clays, &c. (100 feet), and sandstones, clays, &c., with thin coals and limestones (about 80 feet). Other sections were also described. No unconformity has been noticed in Fifeshire between these and the underlying measures. The argillaceous limestones and their coals are fossiliferous; there are a few fish and crustacea, and many plants, with some curious markings, which may be rootlets or perhaps algæ. The last occur only in a limited part of the rock, not with other plants, and are very delicate and membranous. The affinities of these were fully discussed, the author inclining to the view that they are algæ.

February 8.—R. Etheridge, Esq., F.R.S., President,  
in the Chair.

The following communications were read:—

1. "Description of some *Iguanodon* Remains discovered at Brook, Isle of Wight, indicating a New Species, *Iguanodon Seelyi*." By J. W. Hulke, Esq., F.R.S.

2. "On a peculiar Bed of Angular Drift on the high Lower-Chalk Plain between Didcot and Chilton." By Prof. J. Prestwich, M.A., F.R.S., F.G.S.

February 22.—J. W. Hulke, Esq., F.R.S., President,  
in the Chair.

The following communications were read:—

1. "Additional Discoveries of High-level Marine Drifts in North Wales, with Remarks on Driftless Areas." By D. Mackintosh, Esq., F.G.S.

The author begins with remarks on the importance of the marine drift-area (part of which he briefly described in his last paper), especially as regards its great extent, and the absence, so far as yet known, of similar high-level drifts (between 1000 and 1350 feet above the sea) in continental Europe, Asia, or North America. He lately traced the drift-area two miles further south than he had done during former explorations, its entire length being little short of 5 miles. In this paper he gives a detailed description of the numerous exposures of rounded gravel and stratified sand between the north end of Minera Mountain and Llangollen Vale, which in some places spread out into large flat expanses, but more frequently assume the form of knolls (frequently in perched positions), which rise up from beneath a covering of clay or peat. He dwells on the probable origin of the knoll-shaped configuration, including the theory of the precipitation of the drift from the stranding of floating ice, and the forcing-up of previously deposited drift by the same agency, but inclines to the idea of the knolls having been chiefly

accumulated by sea-currents. The author then describes several large areas in North Wales in which he could find no trace of rounded gravel, enters into a consideration of the causes of these driftless areas, and discusses the relative merits of the theory of their having been temporarily occupied by land-ice, and of the theory of non-exposure to tempestuous seas, or seas capable of rounding stones. He then gives an account of the discovery of granite boulders, associated with partially rounded drift, on the summit of Moel Wnion, 1900 feet above the sea (near Aber, North Wales); and endeavours to show that, while they could have been readily transported by floating ice (probably from Scotland, certainly not from Cumberland), the flow of land-ice from Snowdon, according to Ramsay, along the north face of Moel Wnion, must have prevented the access of northern land-ice to the summit of the latter mountain, while land-ice flowing from Cumberland to Anglesey (according to Ramsay) could not have been crossed by land-ice flowing south from Scotland to Moel Wnion. After referring to the outward direction of striæ on the north coast of North Wales, he concludes by giving a summary of facts and inferences.

2. "On some Sections of Lincolnshire Neocomian." By H. Keeping, Esq., of the Woodwardian Museum, Cambridge.

The construction of the Louth and Lincoln railway, in the year 1872, led to the exposure of some fine sections of the Neocomian strata forming the base of the Lincolnshire Wold. From these beds the author had obtained a very large number of fossils, in many cases in an excellent state of preservation. As the sections are now becoming obscure, the author gives an account of the observations made by him at the time when they were best exposed, with lists of the fossils he obtained from them. He agrees with Professor Judd, who in 1867 first described these strata and determined their age, in his conclusions concerning the classification and correlation of the beds, but is disposed to regard the sands above Market Rasen as being a drift deposit, and not as belonging to the Lower Sand and Sandstone.

3. "Notes on the Geology of the Cheviot Hills (English side)." By C. T. Clough, Esq., M.A., F.G.S.

After a brief description of the physical structure of the district, the author passes on to its igneous rocks. These he groups under three heads—(1) the granite, (2) the lava-flows and ash beds, (3) the intrusive dykes. The first occupies an area of about 24 square miles, it varies much in texture, is generally not conspicuously rich in quartz, and often contains hornblende as well as mica. It exhibits in places a curious streaked or banded structure due to local crushing. This is fully described. The lava-flows (with ashes) are porphyrite; this is generally compact, sometimes glassy in structure, with scattered crystals of plagioclase, biotite, hornblende (sometimes augite), a little free quartz, and occasional olivine and apatite. Some peculiarities in these rocks are described. The intrusive dykes

(3) consist of (a) coarse red porphyrite, (b) quartz porphyry, (c) felsite, (d) granite. The author considers that the porphyrite and granite (which are alternately intrusive one in another) belong approximately to the same geological epoch. This is the Lower Old Red Sandstone; and as pebbles of the granite as well as of the porphyrite occur in the Lower Carboniferous measures of the region, great denudation must have taken place prior to the latter epoch. The author also describes some basalt dykes which he considers to be of Miocene age.

March 8.—J. W. Hulke, Esq., F.R.S.,  
President, in the Chair.

The following communications were read:—

1. "Additional Note on certain Inclusions in Granite." By J. Arthur Phillips, Esq., F.R.S., F.G.S.

The author referred to certain rounded inclusions in granite which were rich in mica. These he had described in his paper published in vol. xxxvi. of the 'Quarterly Journal,' and had considered to be contemporaneous segregations from the molten rock. He had, up to that time, not found a case where one of the larger crystals of felspar in a porphyritic granite occurred partly in the one, partly in the other. Of late he had seen several, one of which he described minutely, thus proving the correctness of his supposition.

2. "The Geology of Madeira." By J. S. Gardner, Esq., F.G.S.

Madeira consists almost wholly of sheets of basaltic lava of variable thickness interstratified with tuff scoriæ and red bole, cut by innumerable dykes. In the central part of the island is a horse-shoe-shaped valley, more than 4 miles in diameter, its bed 2500 feet above the sea, its precipitous walls full 3000 feet high, rising here and there to yet greater elevations, and forming a central point in the mountain-system of the island. This the author regards as the basal wreck of a volcanic mountain, blown into the air by an explosion of exceptional violence. Fragments of the slopes of scoriae which once composed the inner shell remain on the peaks surrounding this amphitheatre. The dykes here are trachyte. The author describes a limestone exposed in one place beneath the basalts and referred to the Upper Miocene, and a plant-bearing bed associated with them, containing fossils of species still living in the island, some of which have been wrongly referred to extinct forms. In conclusion the author remarked upon the almost infinite variability of the genus *Rubus* and the difficulty of distinguishing its species.

3. "On the Crag Shells of Aberdeenshire and the Gravel Beds containing them." By Thomas F. Jamieson, Esq., F.G.S.

4. "On the Red Clay of the Aberdeenshire Coast, and the Direction of Ice-movement in that quarter." By Thomas F. Jamieson, Esq., F.G.S.

The author describes a red clay occurring in the eastern part of Aberdeenshire, which differs in many important respects from the



ordinary grey Boulder-clay of the district. Its contents appear to show that it has not been derived from the Jurassic and granitic rocks of Aberdeenshire, but from masses of Old Red Sandstone, now perhaps removed by denudation. Only few and imperfect molluscan remains, with bones of fish, aquatic birds, and seals have been found in this red clay. He regards it as having been formed during a period of great submergence which followed the period of maximum glaciation. He finds at Cove proof of a remarkable change in direction of the flow of the glacial ice. Additional proofs of the submergence are found in the old beaches with shells, extending to heights of from 380 to 470 and even up to 560 feet above the sea-level. The Mollusca occurring in these raised beaches are all of living species, but now occur in arctic seas. He differs from Mr. J. Geikie, who regards these deposits as of post-Glacial age and of estuarine character. He concludes by describing in detail the remarkable section exhibited in the Bay of Nigg.

March 22.—J. W. Hulke, Esq., F.R.S., President,  
in the Chair.

The following communications were read:—

1. "On a Fossil Species of *Camptoceras*, a Freshwater Mollusk, from the Eocene of Sheerness." By Lieut.-Colonel H. H. Godwin-Austen, F.R.S., F.G.S.

2. "Note on the Os Pubis and Ischium of *Ornithopsis eucamerotus* (synonyms—*Eucamerotus*, Hulke; *Bothriospondylus* (in part), R. Owen; *Chondrosteatosaurus*, R. Owen)." By J. W. Hulke, Esq., F.R.S., Pres.G.S.

3. "On *Neusticosaurus pusillus* (Fraas), an Amphibious Reptile having affinities with the terrestrial Nothosauria and with the marine Plesiosauria." By Prof. H. G. Seeley, F.R.S., F.G.S.

April 5.—J. W. Hulke, Esq., F.R.S., President,  
in the Chair.

The following communications were read:—

1. "Geological Age of the Taconic System." By Prof. J. D. Dana, F.M.G.S.

The author takes exception to some remarks made before the Geological Society by Dr. T. Sterry Hunt on the 16th November last. Dr. Sterry Hunt has thrown doubt on the results arrived at by the geologists who have studied the relations of the so-called Taconic strata, not in consequence of any observations of his own, but on the general ground that "where newer strata are in unconformable contact with older ones, the effect of lateral movements of compression, involving the two series, is generally to cause the newer and more yielding strata to dip towards, and even beneath the edge of the older rock—a result due to folds, often with inversion, sometimes passing into faults."

*Phil. Mag.* S. 5. Vol. 13. No. 82. May 1882. 2 F

It was pointed out in opposition to these views, that the observations of Emmons, H. D. and W. B. Rogers, Mather, Sir W. Logan, James Hall, E. Hitchcock, C. H. Hitchcock, Hager, and Wing prove that the Taconic schists and limestones are in conformable succession and of Silurian age. The stratigraphical structure of the Taconic range is, indeed, so simple that all observers who have studied it have described the schists and limestones as conformable; and numerous characteristic Silurian fossils have been found in both. This view had been maintained by Dr. Sterry Hunt himself till 1878, when he first propounded his new interpretation of the strata in question; but the latter was not based on any fresh facts or observations.

The author's own observations on the subject, carried on during many years, were detailed and illustrated by a map of the whole of the Taconic range. In conclusion he pointed out that, even if Dr. Sterry Hunt's general principle were conceded (and he was not by any means himself prepared to make such a concession), it would have no bearing on the point at issue; for the supposed younger strata do not dip against the Taconic schists. In opposition to the view that the geological age of strata can be inferred from their mineral characters, he pointed out what remarkably different rocks have been produced by the metamorphism, in different degrees, of the strata of the Taconic range.

2. "On some Nodular Felsites in the Bala Group of North Wales." By Prof. T. G. Bonney, M.A., F.R.S., Sec.G.S.

These peculiar felsites are chiefly found in one or two localities in the neighbourhood of Bettws-y-coed and of Conway. In the former case, in the same mass are found ordinary compact felsite exhibiting under the microscope fluidal structure, a peculiar rock resembling a greenish schist, and various nodular felsites (with cleavage) showing nodules sometimes 3 or 4 inches in diameter, some being solid, others hollow or more or less filled with chalcidony, chlorite, chalybite, &c. The nodules never exhibit a radial structure; and there is no difference of importance between their structure and that of the ordinary rock. The author showed that the schisty rock is only an amygdaloidal felsite, in which, after cleavage, a secondary (micaceous?) mineral has been deposited along the cleavage-planes. As regards the nodular structure, he showed that it is analogous to the spheroidal structure seen on a larger scale in many igneous rocks, and on a smaller scale in perlite, and gave reasons for its being frequently associated with vesicular cavities. The infiltration of these cavities and consequent solidification was almost certainly prior to the production of the cleavage-surfaces, which are distorted by them. The Conway felsites exhibit similar phenomena, except that they are practically uncleaved.

3. "On the Cambrian (Sedgw.) and Silurian Rocks of Scandinavia." By J. E. Marr, Esq., B.A., F.G.S.

The author has examined the following areas of Cambrian and



XLVIII. *Intelligence and Miscellaneous Articles.*

ON THE DIMENSIONS OF A MAGNETIC POLE IN THE ELECTRO-STATIC SYSTEM OF UNITS. BY PROF. J. D. EVERETT.

A PAPER\* by Clausius, dealing with Electrical and Magnetic Units has just reached me; and I think I shall be doing good service in laying before the readers of the Philosophical Magazine the principal novelty which it contains.

Electricians are familiar with the fact that a circuit with a current flowing in it is a species of magnet, and that the moment of the magnet thus constituted is the product of the current by a certain area.

Hence the moment of a magnet must have the same dimensions as a current multiplied by an area. That is, we must have

$$\text{Pole} \times \text{Length} = \text{Current} \times (\text{Length})^2;$$

or, more simply,

$$\text{Pole} = \text{Current} \times \text{Length}.$$

This equation must be true in any consistent system of units.

In the electrostatic system, the dimensions of Current (or quantity of electricity divided by time) are  $M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-2}$  (M denoting Mass, L Length, and T Time). Hence, by the above equation, the dimensions of a Pole are  $M^{\frac{1}{2}} L^{\frac{5}{2}} T^{-2}$ .

This is substantially Clausius's reasoning, though I have for brevity somewhat altered its form; and it appears to me unimpeachable. Nevertheless the result differs (as the author points out) from Maxwell's formula for the dimensions of a pole in the electrostatic system, namely  $M^{\frac{1}{2}} L^{\frac{1}{2}}$ . This formula will be found in Maxwell's 'Electricity and Magnetism,' § 626, where the name "quantity of magnetism" is used instead of "strength of pole," or the briefer name "pole." It will also be found in the Reprint of Reports of the B.A. Committee on Electrical Standards, page 90; but in neither work have I been able to find an explicit statement of the reasoning by which the result is obtained. Perhaps some reader of the Philosophical Magazine can give the necessary explanation.

In my own treatise on Units† the question at issue is not raised, as practically the dimensions of a magnetic pole do not enter into electrostatic discussions.

The dimensions of a pole, calculated in the ordinary way from the mutual repulsion of two poles, are  $M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-1}$ ; and from this, by considering the force exerted by a current upon a pole, the dimensions of Current in the electromagnetic system are found to be  $M^{\frac{1}{2}} L^{\frac{1}{2}} T^{-1}$ . The relation between these two, it will be observed,

\* "Ueber die verschiedenen Maasssysteme zur Messung electrischer und magnetischer Grössen," von R. Clausius. Vorgetragen 6. März 1882. Separat-Abdruck aus den *Verhandlungen des naturhist. Vereins der preuss. Rheinlande*, Bd. xxxix. [A full translation of this paper will appear in an early Number of this Magazine.—ED.]

† 'Units and Physical Constants' (Macmillan: 1879).

fulfils the foregoing condition,

$$\text{Pole} = \text{Current} \times \text{Length.}$$

It appears to me that Clausius's result must be accepted as the correct one.

Belfast, April 24, 1882.

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#### ON THE ELECTROLYSIS OF DISTILLED WATER.

BY D. TOMMASI.

Several physicists have questioned the possibility of decomposing chemically pure water by means of a galvanic current. According to M. Bourgoïn\*, water is not an electrolyte, the substance mixed with it to render it conductive is alone decomposed.

The few experiments which I have made in regard to this subject have proved to me the contrary—that is to say, that water can be electrolyzed even by the current of a very feeble battery, provided that the calories liberated by the battery are at least equal to those absorbed by water in decomposing into its elements (about 69 calories). Those experiments are as follows:—

(1) Into a U-tube filled with distilled water I introduce two platinum electrodes connected with two Daniell elements. The distance between the electrodes is about 2 centim. No visible effect is produced, even after some time. The calories liberated by the battery are nevertheless more than sufficient to effect the decomposition of the water—in fact,  $98 > 69$ . If, then, the water in this case undergoes no decomposition, that is owing solely to the resistance opposed by it to the passage of the current, and not to insufficiency of energy produced by the battery.

(2) If in the preceding experiment the positive electrode be replaced by a silver wire, this is what is observed:—After 18 hours no appreciable alteration is noticed in the liquid; but if, after taking out the silver wire, a drop of hydrochloric acid be poured into the branch in which it dipped, a very manifest white turbidity makes its appearance, having all the characters of chloride of silver. The hydrochloric acid does nothing more than precipitate the minute quantity of oxide of silver which was dissolved in the distilled water. Now silver does not decompose water at the ordinary temperature; but, in order to produce oxidation, the water must have been decomposed; and consequently the distilled water must have been passed through by the current. The electrodes in this experiment were distant from each other about 7 centim. It is evident, then, that, if the positive electrode is of silver, we can, with the aid of two small Daniell elements, overcome the resistance of a column of distilled water of 7 centim. length.

(3) With three Daniell elements the effect is much more marked. After 15 minutes it can already be ascertained, with the aid of hydrochloric acid, that the silver has begun to dissolve. At the end of 18 hours all the curved portion of the tube is found covered with a coat of oxide of silver, partly reduced by a secondary action.

\* *Ann. de Chem. et de Phys.* [4] xv. p. 47, and xxviii. p. 119.



(4) If, in the experiment I have just spoken of, six Bunsen elements be substituted for the Daniell battery, the decomposition, as might have been expected, takes place with much more intensity. After 18 hours the quantity of oxide of silver, in part reduced, found at the bottom of the tube is relatively considerable.

(5) Gold employed as the positive electrode is not oxidized in the presence of distilled water, even by the action of the current of eight Bunsen elements.

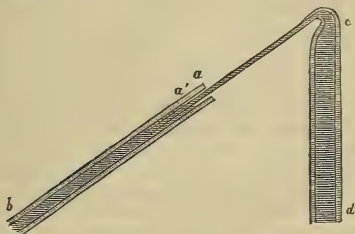
Is silver, then, the only metal which possesses the property of decomposing distilled water under the action of a galvanic current? No, fortunately; for it might be objected to me that, if water is decomposed when silver serves for the positive electrode, it may be due to this—that the oxide of silver, being soluble in water\*, always suffices to render the water sufficiently conductive to be electrolyzed. This objection, however, would not be quite relevant; for it would not account for the current passing at the commencement of the experiment, since at that moment the water contains no foreign substance, and it is only after some time that the silver begins to dissolve. Therefore it is not the oxidation of the silver that permits the current to pass; but it is the current that, by decomposing the water, oxidizes the silver. It is true that, once the water contains a little oxide of silver, its conductivity is increased, and consequently electrolysis can take place with more facility; but, I repeat, the oxidation of the silver is not the determining cause of the decomposition of the water, but only the effect of that decomposition. Be that as it may, here is an experiment which will show positively that the solubility of the silver oxide plays only a secondary part in the electrolysis of distilled water:—

(6) The oxides and the hydrates of copper are completely insoluble in distilled water; and hence they cannot in any way augment the conductivity of the water. Now I have found that copper possesses, like silver, the property of decomposing distilled water when it is connected with the positive pole of a battery. The experiment is made as before; that is to say, a platinum wire and a copper wire are immersed in the two branches of a U-tube filled with distilled water, the former joined to the negative, and the latter to the positive pole of a battery composed of three Daniell elements. The distance separating the two electrodes is about 4 centimetres. At the end of 18 hours, upon a length of about 2 centim. at the lower part a coat of reduced copper is found adhering to the sides of the tube. A portion of the copper is deposited on the platinum wire. The decomposition of the water in this case can be explained only on the hypothesis that the copper employed as the positive electrode tends to diminish the resistance of the water, and consequently to render it more apt to be electrolyzed. It is the same with silver employed as positive electrode.—*Comptes Rendus de l'Académie des Sciences*, April 5, 1882, pp. 948-951.

\* Oxide of silver dissolves in 3000 times its weight of water.

## A LITTLE ILLUSION. BY J. PLATEAU.

Permit me to describe an experiment which, at the first glance, seems as if it must realize perpetual motion. Into a capsule of sufficient dimensions let us pour distilled water till its depth is about 1 centimetre. In this let us immerse one end of a glass tube of small internal diameter, 1·5 millim. for instance, and from 8 to 9 centim. in length; let us keep this tube in a suitably inclined position, so that the water which will be caused to rise in it by capillary action shall occupy a sufficiently large portion of its length. Let us procure a second tube, having, say, an internal diameter of 3 millim., and a length of some centimetres. Let us draw out one end of this second tube, and bend back the drawn-out thin portion so that it makes a more or less acute angle with the wide part. Let us introduce the thin portion into the upper orifice of the inclined tube till it reaches the water contained in this, and give to the wide portion a vertically descending position; this last condition will be obtained by modifying either the above-mentioned angle or the inclination of the other tube. Let us suppose that the orifice of the vertical portion does not reach the liquid of the capsule; lastly, let us imagine the thin portion and the vertical tube both full of water. For greater clearness, I represent in section, in the annexed figure, the upper part of the system.



*ab* is the inclined tube, and *cd* the vertical. In consequence of the narrowness of the space comprised between the slender portion and the inner surface of the tube *ab*, capillarity will maintain the water near the orifice *a* of the latter; suppose that it stops at *a'*. The lower extremity of the tube *cd* not reaching the liquid of the capsule, that tube with its slender portion will constitute a siphon of which the short branch dips in a liquid in equilibrium, while the long branch descends several centimetres lower than the surface of that liquid. Does it not seem, then, that the water must incessantly run through this siphon, to rejoin that in the capsule? Now, if that took place, it would evidently be perpetual motion.

But, the impossibility of perpetual motion being demonstrated, I asked myself what would in reality take place under the above conditions. I therefore requested M. Van der Mensbrugghe to

perform the experiment, which he did according to my directions, employing tubes having the above-assumed dimensions. I pass over in silence the construction of the supports of the tubes, as well as the little manipulations of the experiment: the reader who has the curiosity to repeat it will find out those details for himself. Now we verified that, instead of the water running away through the tube *cd*, it reascends in this, and continues to be aspirated until its free surface reaches a certain point in the slender portion, after which every thing stops. Only, in order that the aspiration may take place, the orifice of the tube *cd* must be several millimetres above the liquid of the capsule; if it is lower, the tube *cd* continues full, the water remains suspended in it.

A little reflection soon enabled me to understand the cause of these apparently singular phenomena. The small surface which terminates at *a'* the liquid between the two tubes is concave in the transverse direction; it therefore, in virtue of its curvature, exerts suction upon the whole mass of liquid to which it belongs—that is to say, upon the liquid of the tube *ab* and that of the tube *cd*, the latter liquid communicating with the former by the slender tube. In the tube *ab* this suction has the effect of keeping the water raised up to *a'*; and it is balanced by the action of gravity, which action is measured by the difference of level between the surface at *a'* and the water of the capsule. In order that it may be in like manner balanced in the tube *cd*, it seems at first necessary that the difference of level between the surface at *a'* and the orifice of the tube *cd* be equal to the preceding, which would require that orifice to reach the water of the capsule; and yet we have seen that equilibrium subsists even when the orifice in question is several millimetres higher. But it is because, in consequence of a tendency to absorption, the water presents at this orifice a slightly concave surface, which exerts a slight suction downwards; and this, added to the incomplete action of gravity, compensates the suction emanating from *a'*. For a greater distance of the orifice from the water of the capsule, the suction at *a'* is in excess, the liquid is drawn upward in the tube *cd*; and this movement stops when the free surface of the liquid has arrived, in the slender portion, at a point where the suction due to its strong concave curvature makes equilibrium with that of *a'*\*. Such is the simple explanation of the observed effects; and this little experiment offers a curious example of the suction exerted by concave liquid surfaces; it shows us, besides, an equally curious exception to the usual action of siphons.

—*Extrait des Bulletins de l'Acad. roy. de Belgique*, Jan. 1882.

\* In our experiment the vertical distance from *a'* to the liquid of the capsule was nearly 4 centim., and the least distance from the orifice of the tube *cd* to the same liquid, for which absorption was produced, was about 5 millim.

THE  
LONDON, EDINBURGH, AND DUBLIN  
PHILOSOPHICAL MAGAZINE  
AND  
JOURNAL OF SCIENCE.

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[FIFTH SERIES.]

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JUNE 1882.

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XLIX. *On the different Systems of Measures for Electric and Magnetic Quantities.* By Prof. R. CLAUSIUS\*.

FOR the measurement of electric and magnetic quantities, it is well known that two essentially different systems, usually called the *electrostatic* and the *electromagnetic*, are employed. Both reduce the determination of electric and magnetic quantities to the measurement of *mass*, *length*, and *time*; but in the manner of the reduction they differ from each other more considerably than is usually the case with other different systems of measures. While in the ordinary mechanical quantities (such as velocities, forces, and mechanical work) the different measuring-systems employed are distinguished from one another only by the so-called fundamental units, viz. the units of mass, length, and time, having different values, in the two above-mentioned systems applied to electricity and magnetism the *formulæ* which serve for the determination of one and the same quantity are also different, since they contain different powers of the fundamental units.

The deduction of these formulæ is systematically carried out with singular completeness in Clerk Maxwell's splendid work, 'A Treatise on Electricity and Magnetism,' Oxford, 1873; and the high estimation in which Maxwell is justly held could not fail to cause his formulæ not only to be accepted in

\* Translated from a separate impression, communicated by the Author, from the *Verhandl. des naturhist. Vereins der preuss. Rheinlande und Westfalens*, vol. xxxix. (1882). Read at the meeting of the Niederrheinische Gesellschaft für Natur- und Heilkunde, on the 6th March, 1882.

England as correct throughout, but also to be adopted unaltered in the works of writers belonging to other nations. In regard to the latter, I will mention only Mascart and Joubert's valuable *Leçons sur l'Electricité et le Magnétisme* (Paris, 1882), and Herwig's useful book, *Physikalische Begriffe und absolute Maasse* (Leipzig, 1880).

Nevertheless I think I can show that Maxwell has committed an error in his development, by which several of his formulæ have been rendered incorrect. The correction of this mistake appears to me to be especially necessary just now, since at the present time the attention of wider circles than formerly is directed to this subject by the decisions of the Congress of Electricians at Paris upon the electrical units of measurement, and hence an error remaining uncorrected might be mischievously disseminated and fixed. It also appears to me that Maxwell's exposition of the subject (which is not all collected together in one passage of his book, but appears in portions in different parts of it) presents some difficulty to the understanding. Hence I think that a connected presentation of the thing, as simple and distinct as possible, will not be unwelcome.

### § 1. *The Fundamental Units and the first General Equation of each System.*

As already mentioned above, the units of mass, length, and time are employed as fundamental units. After Maxwell, it is usual to denote them by enclosing in square brackets the letters which are generally employed to represent those three kinds of quantity. Thus the unit of mass is  $[M]$ , the unit of length  $[L]$ , and the unit of time  $[T]$ .

From these are immediately obtained the units of various other quantities. That velocity with which a unit of length is passed through in the unit of time is employed as the unit of *velocity*; hence, for its representation, we have to divide the unit of length by the unit of time, and we get the formula  $[LT^{-1}]$ . The unit of *force* is that force which imparts the unit of velocity to the unit of mass in the unit of time; hence we obtain the formula which serves to represent it, if we divide the product of the mass-unit and the velocity-unit by the time-unit, whence arises  $[MLT^{-2}]$ . The unit of *mechanical work* is that work which is done by the force-unit along a path equal to the length-unit; and therefore, in order to represent it, we need only to multiply the force-unit by the length-unit, by which we get  $[ML^2T^{-2}]$ .

Now, for the measurement of electricity we must employ



the forces exerted by it. These are of two essentially different kinds:—first, the forces independent of its motion, which amounts of electricity always exert upon one another whether they are at rest or in motion; secondly, the forces arising only through the motion. The former are named the *electrostatic*, and the latter the *electrodynanic* forces. To the *electrodynanic* we must reckon the magnetic forces, if we with Ampère derive the explanation of magnetism from small electric currents taking place in the interior of the magnet. Now, of these two forces, we can apply either the one or the other to the measurement of electricity; and thence arise those two systems of measures, of which the former is called the *electrostatic*, while the latter (as already said) is ordinarily named the *electromagnetic*, but would be more rationally called the *electrodynanic*. In those cases in which it is self-evident that *electrical* systems of measures are meant, one can, for convenience, omit the prefix “electro,” and, briefly, speak of *static* and *dynanic* measuring-systems.

In the *electrostatic* system the most important unit, which serves as the basis of all the others, is the *unit of electricity*. This is determined by the following definition:—*The unit of electricity is that amount of electricity which exerts the unit of force upon an equal amount of electricity at the unit of distance.* We can therefore put the unit of force equal to a fraction having the square of the electricity-unit for its numerator and the square of the length-unit for its denominator. We will at the same time denote, with Maxwell, the electricity-unit by enclosing the letter *e* in square brackets; but, in order to express that the *static* electricity-unit is intended, we will provide the *e* with the index *s*, so that the symbol will have the form [*e<sub>s</sub>*]. The equation in question will then read:—

$$\frac{[e_s^2]}{[L^2]} = [MLT^{-2}];$$

and from this follows

$$[e_s] = [M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-1}]. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In the *electrodynanic* system of measures, it would first suggest itself, from what has been said above, to take as the standard that force which, in addition to the static force, two moved quantities of electricity exert upon each other in consequence of their motion. Respecting this force, however, differences of opinion prevail, which make the choice of it as the starting-point of the determinations inexpedient. On the other hand, the forces exerted upon each other by *closed* electric currents can be regarded as indubitably known. As,

further, the little electric currents which, according to Ampère, must be assumed to flow in the interior of a magnet are likewise closed, we have in magnetism to do with forces of the same kind, and hence we can also select as the standard the force exerted upon one another by two quantities of magnetism. This latter is the most convenient, because magnetic forces can be more simply expressed than the forces exerted between larger closed currents. Accordingly, in the electrodynamic system the unit of magnetism is determined, in precise correspondence with the unit of electricity in the electrostatic system, by the following definition:—*The unit of magnetism is that amount of magnetism which exerts upon an equal amount of magnetism at the unit of distance the unit of force.*

For the mathematical representation, we, again with Maxwell, denote the unit of magnetism by a square-bracketed  $m$ ; but, in order to indicate that the unit in question is the *dynamic* unit, we annex a  $d$  as index, so that the symbol has the form  $[m_d]$ ; and with this we form the equation

$$\frac{[m_d^2]}{[L^2]} = [MLT^{-2}],$$

whence results

$$[m_d] = [M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-1}]. \quad . \quad . \quad . \quad . \quad (2)$$

## § 2. The Relation between Electricity and Magnetism.

By equations (1) and (2), for the static system the unit of electricity, and for the dynamic system the unit of magnetism, are determined. There is now the further question, How is the unit of magnetism to be determined for the static system, and the unit of electricity for the dynamic? For this the well-known proposition of Ampère respecting the substitution for a closed galvanic current of two magnetic surfaces, which has also been adopted by Maxwell in its utmost generality and irrespective of any particular system of measurement\*, is available.

For the sake of simplicity, the current-curve may be supposed plane, and the area of the plane figure inclosed by it assumed as the surface-unit. Besides the plane containing this figure, let us now imagine a parallel plane placed at an infinitesimal distance, and upon this a figure delimited congruent with the first figure and lying perpendicularly opposite to it. Now let these two plane figures be uniformly covered with equal quantities of north and south magnetism—that

\* See Maxwell's 'Treatise on Electricity and Magnetism,' vol. ii. part 3, chapter iii.

which, if we imagine ourselves going with the current round the figures, we have on the left hand with north, and the other with south magnetism. The quantity of the magnetisms is determined by the intensity of the current and the mutual distance of the planes. Let the latter be denoted by  $\epsilon[L]$ , in which  $[L]$ , as always, signifies unit length, and  $\epsilon$  an infinitesimal numerical value. Then, if a current-unit be assumed as the current-intensity, each of the two quantities of magnetism, apart from the sign, is to be supposed equal to a unit of magnetism divided by  $\epsilon$ . The pair of magnetic surfaces thus formed can replace the current in regard to all the forces exerted by it.

To express this mathematically, we have to multiply the intensity of the current by the area round which it flows, to multiply the quantity of magnetism present on one of the surfaces by the distance between the surfaces, and then to equate the two products. Now the current-intensity is a current-unit, which is a unit of electricity flowing through the cross section in unit time, and which is therefore represented by  $[eT^{-1}]$ ; and the area round which it flows is a unit of surface, therefore  $[L^2]$ . Accordingly the first product is  $[eL^2T^{-1}]$ . Further, the quantity of magnetism coming into consideration is  $\frac{[m]}{\epsilon}$ , and the distance between the surfaces  $\epsilon[L]$ ; so that the second product reads  $\frac{[m]}{\epsilon}\epsilon[L]$  or  $[mL]$ . We have consequently to form the following equation:—

$$[mL] = [eL^2T^{-1}],$$

from which results

$$\frac{[m]}{[e]} = [LT^{-1}]. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This equation, which is only an expression of the relation established by Ampère between magnetism and electric currents, must hold good for every system of measurement; and hence we can form from it two special equations referable to the static and the dynamic systems respectively, namely:—

$$\frac{[m_s]}{[e_s]} = [LT^{-1}], \quad . \quad . \quad . \quad . \quad . \quad (3A)$$

$$\frac{[m_d]}{[e_d]} = [LT^{-1}]. \quad . \quad . \quad . \quad . \quad . \quad (3B)$$

If we bring these two equations into connexion with the equations (1) and (2), for  $[e_s]$  and  $[m_d]$ , we thereby arrive

at the expressions for  $[m_s]$  and  $[e_d]$ . From (1) and (3A) we get by multiplication, on which  $[e_s]$  vanishes,

$$[m_s] = [M^{\frac{1}{2}} L^{\frac{1}{2}} T^{-2}]; \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and from (2) and (3B) is obtained by division,  $[m_d]$  vanishing,

$$[e_d] = [M^{\frac{1}{2}} L^{\frac{1}{2}}]. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

### § 3. Maxwell's *Incorrect Equations*.

Instead of the relation between electricity and magnetism deduced in the foregoing section from Ampère's proposition, and expressed in equation (3), in the equations constructed by Maxwell another relation between electricity and magnetism is implicitly expressed; for at page 240 of the second volume of his work, under (1) and (3) are found the equations

$$[pC] = \frac{[L^2 M]}{[T^2]} \quad \text{and} \quad \frac{[e]}{[C]} = [T].$$

Here  $[e]$  signifies, as with us, the unit of electricity, and  $[C]$  represents the unit of current. By  $[p]$  is understood the unit of a quantity which he calls the electrokinetic moment of a current, into the meaning of which, however, we need not here enter, since he himself, further on, puts  $[p] = [m]$ , and therefore we can in the first of the above equations substitute  $[m]$  for  $[p]$ . If we then multiply the two equations together, we obtain the equation

$$[em] = [ML^2 T^{-1}]. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This, according to Maxwell, holds good for every system of measurement; hence in his developments it plays the same part as equation (3) does in ours.

The way in which he arrives at his equation rests upon his bringing into calculation the force exerted by a current upon a magnetic pole, in a similar manner to that in which we, in deducing equations (1) and (2), have brought in the force acting between two units of electricity, and between two units of magnetism, respectively. The force, however, which a current exerts upon a magnetic pole is *electrodynamic*; and from this it follows that an equation of which the deduction is based upon this force can be regarded as valid only in the dynamic system founded upon the electrodynamic forces, and not in the static system based on the electrostatic forces.

Indeed it is also manifest that Maxwell's equation (16) leads to the same result in the dynamic system of measurement as

our equation (3), while in the static system it gives a different result. If, namely, we put, first,

$$[e_d m_d] = [ML^2 T^{-1}];$$

and divide this equation by (2), there comes

$$[e_d] = [M^{\frac{1}{2}} L^{\frac{1}{2}}],$$

which equation agrees with equation (5) above given. But if we put

$$[e_s m_s] = [ML^2 T^{-1}],$$

and divide this by (1), we get

$$[m_s] = [M L], \dots \dots \dots (7)$$

which is different from our equation (4), at which we arrived by employing equation (3).

By Maxwell's incorrect formula for the static magnetism-unit the formulæ of other units in the static system of measures, dependent on the unit of magnetism, have been rendered also incorrect, in a not inexplicable manner.

#### § 4. The Determination of other Units.

The units of electricity and magnetism in both systems of measures having been determined, the units for the other quantities also which occur in electric and magnetic investigations can now be easily deduced. Of these the most important only may here be mentioned.

The unit of the *intensity of a current* results very simply from understanding by current-intensity the quantity of electricity flowing in unit time through a cross section. Hence we only need here to divide the unit of electricity by the unit of time; and we thereby obtain, if  $i$  denotes intensity, the following equations relating to the two systems:—

$$[i_s] = \frac{[e_s]}{[T]} = [M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-2}], \dots \dots \dots (8)$$

$$[i_d] = \frac{[e_d]}{[T]} = [M^{\frac{1}{2}} L^{\frac{1}{2}} T^{-1}]. \dots \dots \dots (9)$$

The unit of *electromotive force* is most simply determined from the condition (which holds universally) that the product from the units of electromotive force, current-intensity, and time, or (what is the same) the product from the units of electromotive force and quantity of electricity, must be equal to the unit of mechanical work. From this, namely, we obtain,



if  $E$  denotes electromotive force, the equation

$$[Ee] = [ML^2T^{-2}]; \quad . \quad . \quad . \quad . \quad (10)$$

and if this equation be brought into the form

$$[E] = \frac{[ML^2T^{-2}]}{[e]},$$

and then applied successively to both systems, the following equations are arrived at:—

$$[E_s] = \frac{[ML^2T^{-2}]}{[e_s]} = [M^{\frac{1}{2}}L^{\frac{1}{2}}T^{-1}], \quad . \quad . \quad (11)$$

$$[E_d] = \frac{[ML^2T^{-2}]}{[e_d]} = [M^{\frac{1}{2}}L^{\frac{3}{2}}T^{-2}]. \quad . \quad . \quad (12)$$

The unit of *resistance* of conductors is defined as the resistance of a conductor in which the unit of electromotive force generates a current of unit intensity. We have, therefore, in order to deduce the formula for it, only to divide the unit of electromotive force by the unit of current-intensity; and then we get, if  $R$  denotes conductors' resistance:—

$$[R_s] = \frac{[E_s]}{[i_s]} = [L^{-1}T], \quad . \quad . \quad . \quad . \quad (13)$$

$$[R_d] = \frac{[E_d]}{[i_d]} = [LT^{-1}]. \quad . \quad . \quad . \quad . \quad (14)$$

Finally, the *capacity* of a conducting body may also be considered, by which is to be understood the quantity of electricity which the body can receive through the action of a unit of electromotive force. Since according to this definition the capacity of a body to which the unit of electromotive force can convey a unit of electricity is to be considered the unit of capacity, in order to construct the formula for the capacity-unit we have to divide the electricity-unit by the unit of electromotive force; and from this we obtain, if  $C$  denotes capacity:—

$$[C_s] = \frac{[e_s]}{[E_s]} = [L], \quad . \quad . \quad . \quad . \quad (15)$$

$$[C_d] = \frac{[e_d]}{[E_d]} = [L^{-1}T^2]. \quad . \quad . \quad . \quad . \quad (16)$$

For the sake of clearness, the units which have been successively determined in the foregoing may here be tabulated:—

## Static Measure.

$$\begin{aligned}
 [e_s] &= [M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-1}], \\
 [m_s] &= [M^{\frac{1}{2}} L^{\frac{5}{2}} T^{-2}], \\
 [i_s] &= [M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-2}], \\
 [E_s] &= [M^{\frac{1}{2}} L^{\frac{1}{2}} T^{-1}], \\
 [R_s] &= [L^{-1} T], \\
 [C_s] &= [L].
 \end{aligned}$$

## Dynamic Measure.

$$\begin{aligned}
 [e_d] &= [M^{\frac{1}{2}} L^{\frac{1}{2}}], \\
 [m_d] &= [M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-1}], \\
 [i_d] &= [M^{\frac{1}{2}} L^{\frac{1}{2}} T^{-1}], \\
 [E_d] &= [M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-2}], \\
 [R_d] &= [L T^{-1}], \\
 [C_d] &= [L^{-1} T^2].
 \end{aligned}$$

## - § 5. Comparison of the Units of the two Systems.

In the foregoing, in determining the static units the measurement based on the electrostatic force, and in determining the dynamic units the measurement based on the electrodynamic force, were employed. The formulæ thus formed can therefore only serve to express the relation in which the units of each system stand to one another, but not to compare, as to their quantity, a unit of one of the systems with the corresponding unit of the other. For this latter purpose the ratio between the electrodynamic and the electrostatic force must also be taken into account.

In the static system the force between two quantities of electricity is expressed simply by the product of the quantities of electricity divided by the square of the distance; while the force between two quantities of magnetism has for its expression in the static system the product of the quantities of magnetism divided by the square of the distance and then multiplied by a constant factor  $k$ , which determines the ratio between the electrodynamic and the electrostatic force. In the case of the quantities of electricity and magnetism considered being assumed as units, the expressions of the two forces are  $[e_s^2 L^{-2}]$  and  $k[m_s^2 L^{-2}]$ .

Now, in order, first, to learn more precisely the nature of the factor  $k$ , we will in the last expression, in accordance with (3A), put for  $[m_s]$  the product  $[L T^{-1}] \cdot [e_s]$ , by which it is changed into  $k[L^2 T^{-2}] \cdot [e_s^2 L^{-2}]$ . Now, as in this expression the last factor  $[e_s^2 L^{-2}]$  represents a force (viz. the unit of force), and the whole expression is also to represent a force, the product  $k[L^2 T^{-2}]$  must be a pure numerical value, whence it follows that  $k$  must be the reciprocal value of the square of a velocity. Consequently, if we choose the symbol  $K$  for the latter, we can write  $k = \frac{1}{K^2}$ , by which, if at the same time we put the formula  $[MLT^{-2}]$ , representing the force-unit, for

$[e_s^2 L^{-2}]$ , we get the following expression for the force exerted by two static units of magnetism upon one another at unit distance:—

$$\frac{[L^2 T^{-2}]}{K^2} [MLT^{-2}].$$

The velocity denoted by  $K$ , which, so far as the measurements hitherto effected permit a judgment to be formed, agrees with the velocity of light *in vacuo*, is a quantity so important for electricity that it seems convenient to introduce a special name for it; and I propose to call it, analogously to a name introduced by Andrews into the theory of heat, the *critical velocity*.

Returning now to the consideration of the magnetic forces, according to the above the force exerted between two static units of magnetism at the unit of distance is equal to the fraction  $\frac{[L^2 T^{-2}]}{K^2}$  of a unit of force. The force between two dynamic units of magnetism at unit distance is, on the contrary, according to § 1, equal to a unit of force. Consequently the latter force is to the former as 1 to  $\frac{[L^2 T^{-2}]}{K^2}$ , or as  $K^2$  to  $[L^2 T^{-2}]$ . Since, then, the forces must at equal distances be as the products of the quantities of magnetism acting upon each other, and consequently in the present case as the square of the dynamic unit of magnetism to the square of the static unit of magnetism, these two squares must also be as  $K^2$  to  $[L^2 T^{-2}]$ , and the two units of magnetism themselves must therefore be as  $K$  to  $[LT^{-1}]$ .

In representing this result mathematically, we must not denote the units of magnetism simply by  $[m_s]$  and  $[m_d]$ ; for these symbols represent the quantities of magnetism under consideration (taken as units) on the hypothesis that the one is measured with the aid of the electrostatic and the other with the aid of the electrodynamic force. For a comparison of the magnitudes of the two units, however, it is necessary that both be measured by the same measure—and consequently that either the dynamic unit be reduced to static measure or the static unit to dynamic measure. For these reduced values we will introduce a special symbol. To indicate that a quantity whose former symbol supposes dynamic measurement is measured according to static measure we will prefix to that symbol *v. s.*, the initials of *valor staticus*; and to indicate that a quantity whose former symbol supposes static measurement is measured according to dynamic measure, we will prefix to that

symbol v. d., the initials of *valor dynamicus*. Thus, v. s.  $[m_d]$  denotes the value measured according to static measure of the dynamic unit of magnetism, and v. d.  $[m_s]$  the value measured according to dynamic measure of the static unit of magnetism.

With the aid of these symbols we can now express the above result as follows:—

$$\frac{\text{v. s. } [m_d]}{[m_s]} = \frac{[m_d]}{\text{v. d. } [m_s]} = \frac{K}{[LT^{-1}]}. \quad . \quad . \quad (17)$$

In accordance with this, and employing the before-given formulæ for  $[m_s]$  and  $[m_d]$ , the following two pairs of equations for the two systems of measurement can be formed:—

$$[m_s] = [M^{\frac{1}{2}} L^{\frac{5}{2}} T^{-2}]; \quad \text{v. s. } [m_d] = [M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-1}] K; \quad . \quad (18)$$

$$\text{v. d. } [m_s] = [M^{\frac{1}{2}} L^{\frac{5}{2}} T^{-2}] K^{-1}; \quad [m_d] = [M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-1}]. \quad . \quad . \quad (19)$$

From these equations corresponding equations for the units of the other quantities can also be derived.

As to the quantity  $e$ , we can put, in accordance with (3A) and (3B),

$$[e_s] = [m_s] [L^{-1} T], \quad [e_d] = [m_d] [L^{-1} T],$$

and hence also

$$\text{v. d. } [e_s] = \text{v. d. } [m_s] [L^{-1} T], \quad \text{v. s. } [e_d] = \text{v. s. } [m_d] [L^{-1} T].$$

By employing these values we obtain from the preceding equations:—

$$\frac{\text{v. s. } [e_d]}{[e_s]} = \frac{[e_d]}{\text{v. d. } [e_s]} = \frac{K}{[LT^{-1}]}, \quad . \quad . \quad . \quad . \quad . \quad (20)$$

$$[e_s] = [M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-1}]; \quad \text{v. s. } [e_d] = [M^{\frac{1}{2}} L^{\frac{1}{2}}] K, \quad . \quad (21)$$

$$\text{v. d. } [e_s] = [M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-1}] K^{-1}; \quad [e_d] = [M^{\frac{1}{2}} L^{\frac{1}{2}}]. \quad . \quad (22)$$

From these equations we get for  $i$ , conformably with (8) and (9):—

$$\frac{\text{v. s. } [i_d]}{[i_s]} = \frac{[i_d]}{\text{v. d. } [i_s]} = \frac{K}{[LT^{-1}]}, \quad . \quad . \quad . \quad . \quad . \quad (23)$$

$$[i_s] = [M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-2}]; \quad \text{v. s. } [i_d] = [M^{\frac{1}{2}} L^{\frac{1}{2}} T^{-1}] K, \quad . \quad (24)$$

$$\text{v. d. } [i_s] = [M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-2}] K^{-1}; \quad [i_d] = [M^{\frac{1}{2}} L^{\frac{1}{2}} T^{-1}]. \quad . \quad (25)$$

For  $E$  we get, from the equations for  $e$  in conjunction with equations (11) and (12):—

$$\frac{\text{v. s. } [E_d]}{[E_s]} = \frac{[E_d]}{\text{v. d. } [E_s]} = \frac{[LT^{-1}]}{K}, \quad . \quad . \quad . \quad (26)$$

$$[E_s] = [M^{\frac{1}{2}} L^{\frac{1}{2}} T^{-1}]; \text{ v. s. } [E_d] = [M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-2}] K^{-1}, \quad (27)$$

$$\text{v. d. } [E_s] = [M^{\frac{1}{2}} L^{\frac{1}{2}} T^{-1}] K; \quad [E_d] = [M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-2}]. \quad (28)$$

For R there result from the equations for E and  $i$  in conjunction with equations (13) and (14):—

$$\frac{\text{v. s. } [R_d]}{[R_s]} = \frac{[R_d]}{\text{v. d. } [R_s]} = \frac{[L^2 T^{-2}]}{K^2}, \quad . . . \quad (29)$$

$$[R_s] = [L^{-1} T]; \quad \text{v. s. } [R_d] = [L T^{-1}] K^{-2}, \quad (30)$$

$$\text{v. d. } [R_s] = [L^{-1} T] K^2; \quad [R_d] = [L T^{-1}]. \quad (31)$$

Lastly, for C we get from the equations for  $e$  and E in conjunction with equations (15) and (16):—

$$\frac{\text{v. s. } [C_d]}{[C_s]} = \frac{[C_d]}{\text{v. d. } [C_d]} = \frac{K^2}{[L^2 T^{-2}]}, \quad . . . \quad (32)$$

$$[C_s] = [L]; \quad \text{v. s. } [C_d] = [L^{-1} T^2] K^2, \quad (33)$$

$$\text{v. d. } [C_s] = [L] K^{-2}; \quad [C_d] = [L^{-1} T^2]. \quad (34)$$

#### § 6. *Maxwell's Statements respecting the Ratios between the Static and Dynamic Units.*

On the ratios between the static and dynamic units, discussed in the foregoing section, Maxwell expresses himself differently. He gives, in his work on Electricity (vol. ii. p. 243), the following table, in which I have merely taken leave to alter the letters employed for the notation so as to make them agree with our notation:—

*Number of Electrostatic Units in one Electromagnetic Unit.*

For $e$ and $i$	. . . . .	K,
„ $m$ and E,	. . . . .	$\frac{1}{K}$ ,
„ C	. . . . .	$K^2$ ,
„ R	. . . . .	$\frac{1}{K^2}$ .

Among these statements, that which refers to the magnetism  $m$  directly contradicts our equation (17), since with Maxwell K stands in the denominator, while in equation (17) K stands in the numerator. The mistake made by Maxwell in this statement is a consequence of the already mentioned oversight made by him in the construction of the expression for the electrostatic unit of magnetism.



With respect to the rest of the statements, I think I must make one remark upon their form. I cannot admit it to be mathematically correct to say that the number of the electrostatic units in an electromagnetic (or electrodynamic) unit is equal to a *velocity* or to any power of a *velocity*. It is true that Maxwell himself has, in another passage, somewhat modified his manner of expression by adding the word "numerically" to the word "equal;" but other authors, who have followed him in treating of the units, have paid no particular regard to this addition, but have simply retained the above form, to which they have thereby given wide diffusion.

A manner of expression of this sort permits it to be inferred that formulæ of different dimensions in respect of their quantity are compared with one another, which is inadmissible. If one wishes to compare a static unit with the corresponding dynamic unit with respect to quantity, one must, as we have above done, express both in one and the same system of measures, and consequently either reduce the dynamic unit to static measure or the static unit to dynamic measure. Thereby are obtained formulæ of equal dimensions; and when these are compared with one another, it is found, not that the number of static units is equal to a *velocity* or to a power of a *velocity*, but that it is equal to the *ratio of two velocities*, or equal to a power of that *ratio*.

I believe that in investigations like that with which we are here occupied, in which it is precisely the determination of the dimensions of the different kinds of quantities that is chiefly the question, it is essentially important that even the manner of expression in regard to the dimensions be absolutely correct.

### § 7. *The Practical System of Measures.*

In all that has been said hitherto the question has been only, how can the units relating to electricity and magnetism be represented by the fundamental units, namely the units of mass, length, and time? The quantity which has been given to the fundamental units must now be discussed.

Gauss and Weber, who introduced the electrodynamic system of measures, selected as the units of mass, length, and time the milligram, millimetre, and second; while the British Association (who in the rest have adopted the system of Gauss and Weber) have, at the suggestion of Sir William Thomson, chosen the gram, centimetre, and second as units of mass, length, and time.

Both systems of fundamental units, however, furnish electrical units the magnitude of which is very different from the

magnitudes to be practically measured ; so that the latter can only with the aid of very large or very small numerical values be represented by those units. To avoid this inconvenience, the British Association, and in connexion with it the Congress of Electricians at Paris, have decided to multiply or divide the electrical units resulting from Thomson's system of fundamental units by certain (some of them very high) powers of 10, and thus to form units of practically suitable magnitude.

For these latter, names borrowed from celebrated men specially meritorious with respect to this branch of physics were then chosen. Among the units we have above discussed, only one is left without a name, and, indeed, just that which forms the base of the dynamic system, namely the unit of magnetism. Hence I would take leave to propose that for it the name "weber" be introduced ; for to Weber we are indebted for singularly great advances in regard to electrical measurements, and he, in conjunction with Gauss, was the founder of the electrodynamic system. Hence also, formerly, one of the units, the unit of current-intensity, was designated by his name. In the practical system now introduced, however, it turned out that the unit of current-intensity which fits into this system differs from that designated by the name of Weber in the proportion of 1 to 10; and as it was feared that confusion might be produced by employing the same name for the new unit, another name, ampère, was given to it. Accordingly, if the name of Weber were not introduced for the unit of another kind of quantity, it would be missing in the system of names, which would not be in keeping with justice. I therefore think I may reckon upon my proposal meeting with general assent.

The practical system of measures established by the Congress of Electricians, with the inclusion of the above-discussed unit of magnetism, if the gram and the centimetre be, as is usual, denoted by *gr* and *cm* and the second by *s*, can be written as follows:—

$$\text{Weber} \dots\dots [m_d] = gr^{\frac{1}{2}} cm^{\frac{3}{2}} s^{-1} \cdot 10^8,$$

$$\text{Coulomb} \dots [e_d] = gr^{\frac{1}{2}} cm^{\frac{1}{2}} \cdot 10^{-1},$$

$$\text{Ampère} \dots\dots [i_d] = gr^{\frac{1}{2}} cm^{\frac{1}{2}} s^{-1} \cdot 10^{-1},$$

$$\text{Volt} \dots\dots\dots [E_d] = gr^{\frac{1}{2}} cm^{\frac{3}{2}} s^{-2} \cdot 10^8,$$

$$\text{Ohm} \dots\dots\dots [R_d] = cm s^{-1} \cdot 10^9,$$

$$\text{Farad} \dots\dots [C_d] = cm^{-1} s^2 \cdot 10^{-9}.$$

§ 8. *The Practical System of Measures as a Simple System.*

In the foregoing form the practical system has the inconvenience that with every unit one must bear in mind the power of 10 by which the general formula given in § 4 is to be multiplied. Nevertheless, as the Committee of the British Association has already remarked, by a suitable selection of the fundamental units the practical can be made a simple system, in which all the units can be represented merely by the formulæ given in § 4. For this purpose  $1 \cdot 10^{-11}gr$  must be taken as the unit of mass, and  $1 \cdot 10^9cm$  or  $1 \cdot 10^7m$  as the unit of length, while the time-unit remains 1 second.

If the length  $1 \cdot 10^7m$  be denoted by  $q$  to indicate that it is equal to a quadrant of the meridian, and the mass  $1 \cdot 10^{-11}gr$  by  $p$ , the practical units can be written as follows:—

$$\text{Weber} \dots\dots [m_a] = p^{\frac{1}{2}} q^{\frac{3}{2}} s^{-1},$$

$$\text{Coulomb} \dots\dots [e_a] = p^{\frac{1}{2}} q^{\frac{1}{2}},$$

$$\text{Ampère} \dots\dots [i_a] = p^{\frac{1}{2}} q^{\frac{1}{2}} s^{-1},$$

$$\text{Volt} \dots\dots [E_a] = p^{\frac{1}{2}} q^{\frac{3}{2}} s^{-2},$$

$$\text{Ohm} \dots\dots [R_a] = q s^{-1},$$

$$\text{Farad} \dots\dots [C_a] = q^{-1} s^2.$$

This manner of representing them has manifestly the advantage of greater simplicity; and at the same time it is further to be remarked that the units of other kinds of electric and magnetic quantity, not contained in the preceding table, assume a similar simple form when these fundamental units are employed; while if  $gr, cm, s$  be used, the formula of every new unit must be provided with a specially to be determined power of 10 as a factor, by which the distinctness and ready intelligibility of the formulæ are impaired.

The circumstance that, in order to obtain at once for electric units values agreeing to some extent with the quantities we have at other times to measure, and hence convenient for us, so very small a unit of mass and so very large a unit of length must be employed, is to be regarded as a characteristic peculiarity of electricity, and hence cannot be avoided. In order, then, to facilitate the representation in investigations in which such very small and very large units occur, it is desirable to be able to state them briefly, not only by mathematical symbols, but also in words; and I would make a proposal for that purpose.

In the French system of weights and measures, as is well known, for each kind of quantity, starting from the funda-

mental unit, the first three lower units resulting from divisions by ten are named by prefixing the words *deci*, *centi*, and *milli*, borrowed from the Latin, and the first four higher units, resulting from multiplications by ten, by prefixing the words *deka*, *hekto*, *kilo*, and *myria*, borrowed from the Greek. I propose, then, to employ for naming the lower units arising from further divisions by 10, and the higher units arising from multiplications by ten, likewise Latin and Greek numerals, but *ordinal* numerals, which will specify the negative or positive exponents of the powers of ten by which the fundamental unit is to be multiplied; so that, for instance, with the metre the fifth lower unit  $1 \cdot 10^{-5}m$  will be called a *quintometre*, and the fifth higher unit  $1 \cdot 10^5m$  a *pentometre*, and correspondently with the gram and other fundamental units\*.

According to this, we have to call the mass  $1 \cdot 10^{-11}gr$ , occurring in the above system, an *undecimogram*, and the length  $1 \cdot 10^7m$  a *hebdometre*. The practical system of measures is consequently characterized in its entirety by the name *the electrodynamic system of measures undecimogram, hebdometre, second*. This name easily impresses itself in the memory; and by it the aim of a more precise definition of the system is more perfectly attained than by saying that it is the *electrodynamic system of measures gram, centimetre, second*, in which, however, each unit must be multiplied by a specially to be stated power of ten.

### § 9. The Critical System.

We have seen, in section 5, that, in the different kinds of electric and magnetic quantity, the ratio of the dynamic unit to the value of the static unit measured according to dynamic measure, or, what comes to the same, the ratio of the value of the dynamic unit measured according to static measure to the static unit, is always represented by a power of the ratio of the critical velocity to the velocity-unit. It thence follows that, if the fundamental units be chosen so that the velocity-unit becomes equal to the critical velocity, then those ratios become each equal to 1. A system of measures in which this

\* Only the higher unit resulting from multiplication by  $10^6$  makes a little difficulty. As the sixth is *ἑκτος* in Greek, in accordance with the above we should have, properly, to call the quantity  $1 \cdot 10^6m$  a hectometre. But in the French system of measures the prefix *hekto* is already employed in another sense, namely as a contraction of *ἑκατόν*, so that *hekto-mètre* signifies  $100m$ ; and we must therefore seek help from some other source for the naming of  $1 \cdot 10^6$ . To that end we might, *e. g.*, deviating somewhat from Greek usage, say *hexometre*, or even employ the prefix *mega*, proposed for this order of quantity by the British Association, and form the name *megametre*,

takes place will, as has been insisted by other authors, be distinguished above the rest by simplicity. Such a one may here, in conclusion, be discussed.

First, as to the time-unit to be employed in the new system, this can be selected at pleasure; but, since all the systems hitherto considered agree in having a second as the unit of time, there is no reason for choosing any other time-unit here, and we therefore retain the second.

By this determination of the time-unit the unit of length is also determined, because as such that length must be taken which a point endowed with the critical velocity would travel in one second. This amounts to approximately 30 meridian-quadrants, and is consequently about 30 times the unit of length of the practical system of measures. We will denote it by  $\lambda$ .

There still remains to be determined the unit of mass. This has no influence upon the unit of velocity; so that any value whatever can be given to it without altering the unit of velocity; hence it appears to me most expedient so to choose this value that two of the most important electrical units, viz. those of quantity of electricity and intensity of current, take the same values in the new system of measures as in the practical system. In the latter we have, according to the preceding section, to put

$$[e_d] = p^{\frac{1}{2}} q^{\frac{1}{2}} \text{ and } [i_d] = p^{\frac{1}{2}} q^{\frac{1}{2}} s^{-1};$$

and in the new system, if its unit of mass be denoted by  $\mu$ , the following equations must hold:—

$$[e_d] = \mu^{\frac{1}{2}} \lambda^{\frac{1}{2}}; \text{ and } [i_d] = \mu^{\frac{1}{2}} \lambda^{\frac{1}{2}} s^{-1}.$$

Now, if the latter values of  $[e_d]$  and  $[i_d]$  are to agree with the former, the products  $\mu^{\frac{1}{2}} \lambda^{\frac{1}{2}}$  and  $p^{\frac{1}{2}} q^{\frac{1}{2}}$  must be equal, and hence also

$$\mu \lambda = p q, \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

from which follows

$$\mu = p \frac{q}{\lambda}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

Hereby the determination of  $\mu$  is reduced to the determination of  $\lambda$ , and consequently to the determination of the critical velocity; and from what has been said above respecting the approximate value of  $\lambda$ , it results that  $\mu$  is approximately  $\frac{1}{30}$  undecimogram or  $\frac{1}{3}$  duodecimogram—that is, a three billionth of a gram.



This system, in which the velocity-unit is equal to the critical velocity, may be called the *critical system of measures*; and here the values corresponding to it of the electric and magnetic units may also be collected:—

$$[m_d] = \text{v. d. } [m_s] = \mu^{\frac{1}{2}} \lambda^{\frac{3}{2}} s^{-1} = \frac{\lambda}{q} \text{ weber,}$$

$$[e_d] = \text{v. d. } [e_s] = \mu^{\frac{1}{2}} \lambda^{\frac{1}{2}} = 1 \text{ coulomb,}$$

$$[i_d] = \text{v. d. } [i_s] = \mu^{\frac{1}{2}} \lambda^{\frac{1}{2}} s^{-1} = 1 \text{ ampère,}$$

$$[E_d] = \text{v. d. } [E_s] = \mu^{\frac{1}{2}} \lambda^{\frac{3}{2}} s^{-2} = \frac{\lambda}{q} \text{ volt,}$$

$$[R_d] = \text{v. d. } [R_s] = \lambda s^{-1} = \frac{\lambda}{q} \text{ ohm,}$$

$$[C_d] = \text{v. d. } [C_s] = \lambda^{-1} s^2 = \frac{q}{\lambda} \text{ farad.}$$

Although this critical system of measures is not suited for practical measurements, and especially for the preparation of standards, because the critical velocity is not yet known with sufficient precision, yet it may offer great conveniences in theoretic investigations, on account of the accordance between the values of the static and dynamic units.

L. *On the Question of Electrification by Evaporation.* By S. H. FREEMAN, *Fellow in Physics, Johns Hopkins University, Baltimore, Md.\**

IT has been very commonly believed that evaporation is an important source of atmospheric electricity. So far as this belief has an experimental basis, it is to be found in the researches of Pouillet† and of Tait and Wanklyn‡. In comparison with their work the experiments of Volta, Saussure, and others are of little value. As the result of an elaborate series of experiments, Pouillet came to the following conclusions:—

1. Simple changes of state never give the least sign of electrification.

\* Communicated by the Author.

† *Annales de Chimie et de Physique*, sér. 2, tome xxxv. p. 401, and xxxvi. p. 4.

‡ *Phil. Mag.* ser. 4. vol. xxiii. p. 494.

2. From solutions of alkaline solids the water evaporated carries away a negative charge.

3. From solutions of gases, acids, or salts the water carries off a positive charge.

Tait and Wanklyn repeated Pouillet's experiments with a more sensitive electrometer. They detected electrification where Pouillet had failed to do so, *e. g.* in the evaporation of distilled water; and in some other cases the effects obtained were totally different in kind and degree from those obtained by Pouillet and earlier experimenters.

In these experiments a few drops of liquid were dashed on a red-hot platinum dish insulated and connected with an electrometer. So long as the spheroidal state continued, little or no electrification was observed; but as soon as violent vaporization began, decided deflections were obtained. This fact and other circumstances about the experiments indicate that friction was the chief source of electrification, and make it doubtful whether evaporation had any part in producing the observed electrification. Tait and Wanklyn recognized the fact that to friction was due a large part of the electrification which they obtained. Still, in his lectures on Thunderstorms\*, Professor Tait, speaking of atmospheric electricity, says:—"In calm clear weather the atmospheric charge is usually positive. This is very commonly attributed to evaporation of water; and I see no reason to doubt that the phenomena are closely connected." After reading these lectures, the writer of this article decided to investigate whether evaporation alone and under normal conditions causes electrification, and whether such electrification, if any, is sufficient to account for the phenomena of atmospheric electricity. In this connexion it will be remembered that Faraday traced the electricity, produced by the escape of steam or water from orifices, to friction, and concluded it was not due to evaporation, nor did it have any bearing on atmospheric electricity.

The investigation was begun with the expectation, on the part of the writer, of finding electrification; Prof. Rowland, to whom the author is much indebted, believed that no electrification would be found. In any case the subject seemed important enough to warrant experiments, which were free from the objections which hold against those already described. At the very beginning of the investigation it was found that at most the electrification due to evaporation would be extremely small, and very great caution would be necessary to eliminate various sources of error. The apparatus finally used

\* 'Nature,' vol. xxiii. p. 340.

consisted of an evaporating-dish, 19 centim. in diameter and 1 centim. deep, insulated, and connected with one pair of quadrants of a Thomson's quadrant-electrometer. The other pair of quadrants and the case of the electrometer were connected with earth. The evaporating-dish was supported on a wire frame suspended by silk threads. To prevent disturbances due to electricity on neighbouring objects, particularly the clothes of the observer, it was found necessary to enclose the whole apparatus in a metallic case. Openings were made in this case, to facilitate evaporation and to permit the mirror of the electrometer to be seen. The commutator was governed by a silk thread passing through an opening in the case. In the experiments the results of which are given in Table II., the evaporating-dish was of copper; in the other cases it was of tin. The liquids examined were alcohol, sulphuric ether, water, and solutions of NaCl and of  $\text{CuSO}_4$ . The last three were most carefully studied—water and NaCl because of their importance in evaporation in nature, and  $\text{CuSO}_4$  because of the very large deflections which Tait and Wanklyn obtained with it.

The electrometer was about thirteen times as sensitive as Prof. Tait's. Its deflections were reduced to absolute measure by comparison with a Daniell's cell, the deflections produced by which were observed before and after each series. The capacity of the evaporating-dish and its connexions was found, by comparison with Prof. Rowland's standard condenser, to be 65 centim. nearly. The rate of evaporation was determined by weighing the evaporating-dish and liquid before and after each series. It was found impossible to eliminate every source of electricity except evaporation, since deflections were always obtained even with the evaporating-dish dry. In order to correct for this, each series began and ended with two or more observations of the deflections obtained by insulating for a known time, usually five minutes, the dry evaporating-dish. Between these observations, several similar observations with the liquid evaporating were made.

As the result of a large number of observations, in which the evaporating-dish was insulated for five minutes,

Alcohol gave a potential from . . . . .	} —0·04 to —0·09	that of a Daniell's	[cell.
Cotton wet with alcohol gave a potential from			
Sulphuric ether gave a potential from . . . . .	} +0·02 to —0·06	" "	"
potential from . . . . .			
	} —0·02 to —0·10	" "	"

(The sign indicates the charge apparently carried away by the vapour.)

No correction has been made in the above figures for the deflections obtained with the dry dish. These were more variable, but usually of the same sign as when a liquid was evaporating, and of a magnitude not very different. Making this necessary correction,

Alcohol gave a potential from . . . . .	} -0.024 to -0.065 that of a Daniell's [cell,
Cotton wet with alcohol gave a potential from	
Sulphuric ether gave a potential from . . . . .	
	} -0.028 to -0.050      "      "
	} -0.004 to -0.023      "      "

In the above observations the rate of evaporation was not measured.

The earlier observations on water and salt water gave deflections about 0.1 that given by a Daniell's cell, the deflections with the dry dish being nearly the same (see Table I.). Though the dish was insulated for five minutes or more, the position of the spot of light was read every thirty seconds. Far the greater part of the deflection was attained in the first minute or two; and after five minutes scarcely any further deflection could be discovered.

The observations thus indicated that the small deflections obtained were mainly due to leakage from electrified parts of the apparatus. The sources of this leakage were carefully investigated; and three principal ones were discovered, viz. the charged needle of the electrometer, the vulcanite posts supporting the electrodes of the electrometer, and the glass cup of the commutator. In the later experiments care was taken to eliminate these sources of leakage as far as possible. The connexions were so made that the electrodes and commutator were not touched for days before the experiments, and the charge on the needle was not replenished within about twenty-four hours of the experiment. When these precautions were taken the deflections became less than 0.01, and generally less than 0.005 of a Daniell's cell (see Table II.).

In contrast with these deflections, Tait and Wanklyn obtained, by dashing liquids on red-hot platinum, for

solution $\text{CuSO}_4$	a potential	+ 300	times that of a Daniell's cell,
solution $\text{NaCl}$	"      "	+ 120	"      "      "      "
distilled water	"      "	+ 24	"      "      "      "
alcohol	"      "	+ 3	"      "      "      "

In order to compare the deflections obtained by evaporation with those obtained by friction, the experiments of Tait and Wanklyn were repeated. It was impossible, however, to measure the deflections obtained, since in almost every case, as soon as the spheroidal state ceased, the spot of light went beyond the limits of the scale.

To show the sensitiveness of the apparatus to very slight friction, it was so arranged that drops of liquid could fall upon the evaporating-dish from an insulated conductor in metallic connexion with it. A few drops of liquid falling three or four centimetres were sufficient to give deflections of nearly the size obtained from a Daniell's cell, and much larger than any obtained in evaporation.

In order to compare the results obtained with the phenomena of atmospheric electricity, the writer computed the virtual depth of water which would be necessary to produce one flash of lightning if the vapour in a thunder-cloud had been electrified as indicated by the experiments. By virtual depth is meant the depth of the layer of water over the whole area of the cloud, were all its vapour condensed to the liquid state.

Let  $\Delta$  = this depth in centimetres for a cloud of area  $A$  and height  $a$ ,

$V$  and  $C$  = respectively the potential and capacity of the cloud,

$q$  = the charge per gramme of water ;

then

$$\Delta = \frac{VC}{Aq}.$$

But, from Sir Wm. Thomson's experiments,  $V = 130a^*$ ; and by the ordinary formula for a condenser of horizontal plates,

$$C = \frac{A}{4\pi a}.$$

Now, in the experiments,

let  $d$  = the deflection obtained by insulating for  $t$  minutes, and apparently due to evaporation,

$D$  = the deflection obtained from a Daniell's cell,

$W$  = weight, in grammes, of liquid evaporated in  $T$  minutes,

$v$  and  $c$  = potential and capacity of evaporating-dish and its connexions ;

\* Papers on Electricity and Magnetism, p. 259.



then

$$q = \frac{v c T}{t W}.$$

But  $c = 65$  centimetres, as stated above; and  $v = 0.00374 \frac{d}{D}$  in electrostatic units, according to Sir William Thomson's measurements\*. Then

$$\Delta = 43 \frac{t W D}{T d},$$

in terms of the original measurements in the experiments,

TABLE I.

Showing Results of earlier Series.

Liquid.	Deflection with evapo- ration.	Deflection with dry dish.	$d$ , in scale- divisions.	$D$ , in scale- divisions.	$t$ , in minutes.
Distilled water .....	4.12	4.60	+0.48	42.02	5
	4.82	4.33	-0.49	42.05	5
	3.95	4.50	+0.55	41.55	5
	2.48	2.33	-0.15	42.00	5
Solution NaCl .....	6.70†	4.68	-2.02	41.75	5
	3.47	4.40	+0.93	41.50	5
	3.10	3.94	+0.84	42.20	5

Liquid.	$T$ , in minutes.	$W$ , in grammes.	$\Delta$ , in centi- metres.	Sign of appa- rent charge of vapour.
Distilled water .....	43	1.44	630	+
	43	0.49	210	-
	37	0.54	237	+
	41	0.80	1170	-
Solution Na Cl .....	55	0.29	24	-
	54	0.48	85	+
	39	0.70	194	+

\* Papers on Electricity and Magnetism, p. 245.

† Throughout this series there was an instantaneous deflection at breaking contact, which was several times larger than the total deflection obtained during the five minutes' insulation. The series is therefore of much less value than any of the others, in which the instantaneous deflection was never more than 0.1 of a division.

TABLE II.  
Showing Results of later Series.

Liquid.	Deflection with evapora- tion.	Deflection with dry dish.	$d$ , in scale- divisions.	$D$ , in scale- divisions.
Saturated solution $\text{CuSO}_4$	0.3	0.0	+0.30	37.6
	0.12	0.6	+0.60	37.6
	0.8	0.6	+0.20	37.6
	0.6	0.42	+0.18	39.6
	0.5	0.21	+0.29	39.6
	0.1	0.21	-0.11	39.6
Saturated solution $\text{NaCl}$	0.3	0.21	+0.09	39.6
	0.0	0.35	-0.35	39.6
	0.2	0.12	+0.08	39.6
	0.4	0.35	+0.05	39.6
Hydrant water .....	1.6	0.6	+1.00	37.6
	1.45	0.6	+0.85	37.6
Distilled water .....	1.3	0.6	+0.70	37.6
	0.5	0.6	-0.10	39.6
Cotton wet with hydrant water .....	1.0	0.66	+0.34	37.6

Liquid.	$t$ , in minutes.	$T$ , in minutes.	$W$ , in grammes.	$\Delta$ , in centi- metres.	Sign of apparent charge of vapour.
Saturated solution $\text{CuSO}_4$	2	174	3.19	198	+
	2	174	3.19	99	+
	10	174	3.19	1482	+
	10	38	0.9	2240	+
	5	38	0.9	695	+
	5	38	0.9	1833	-
Saturated solution $\text{NaCl}$	5	38	0.9	2240	+
	6	30	0.54	525	-
	2	30	0.54	766	+
	6	30	0.54	3678	+
Hydrant water .....	10	30	0.59	318	+
	10	30	0.59	373	+
	10	30	0.59	454	+
Distilled water .....	7	35	0.89	3031	-
Cotton wet with hydrant water .....	11	30*	0.59*	1029	+

The actual value of  $\Delta$  (the virtual depth of water) for a cloud 1500 metres thick, if condensation began at

35° C., is about 5.9 centim.

30 " " 4.5 "

25 " " 3.4 "

20 " " 2.6 "

15 " " 1.9 "

\* In this case the rate of evaporation was not measured, but was assumed in computing  $\Delta$  to be the same as for hydrant water at the same time. The rate was probably greater, which would make  $\Delta$  still greater.

Hence, even if the deflections  $d$  of the tables be really due to evaporation, and if evaporation be the principal source of the atmospheric electricity, the quantity of water which would be required to produce a single flash of lightning is very much greater than the actual quantity ever found in a thunder-cloud, while the thunder-cloud usually gives, not one, but many flashes.

It may be objected to this reasoning that a thunder-cloud in some way collects the electricity obtained by the evaporation of a much larger quantity of water than that contained in itself. On this account it is of interest to consider the total evaporation on the globe. If 100 centim. be taken as the average annual rainfall for the whole surface of the earth, and 400 centim. be taken as the value of  $\Delta$ , the total annual evaporation on the earth is sufficient to produce only about 14,000,000 flashes of lightning from clouds 9 square kilometres in extent. Hence, if one were able to observe every flash of lightning which occurs within 18 kilometres of himself, the average number of lightning-flashes seen by such observers at different points of the earth's surface in one year would be only twenty-eight. Calculation from more exact data would give a less number. This calculation assumes that all the electricity is discharged through lightning-flashes, whereas a very large portion of the atmospheric electricity is discharged in other ways—*e. g.* in the aurora borealis and other atmospheric phenomena which are referred to electricity, and in quiet discharges which take place without any noticeable accompanying phenomena.

Evaporation is then, at most, a very insignificant source of the atmospheric electricity. But, further, the following facts are to be observed :—

1. The deflections obtained in the experiments were always very small. (In the original readings it was easy to make an error of 0.1 of a division; and though the numbers in the tables are the means of several observations, they are still affected by this error of reading.)
2. The sign of the apparent charge is not always the same for the same liquid. This is particularly noticeable in the important case of water.
3. The deflections were very much diminished when care was taken to eliminate very small sources of electricity. Still the deflections obtained with the evaporating-dish dry, are usually much larger than the difference between these and the deflections obtained when a liquid was evaporating.

Evidently, then, most of the electrification was due to other causes than evaporation; and the experiments do not certainly

trace any electricity whatever to this source. The problem of the source of the electricity of the atmosphere is still unsolved. Evaporation, first proposed by Volta, whose theory until now has been better supported by experiment than any other, fails to account even for a small portion of it; and no other source has been proposed which can yet be considered sufficient.

II. *On the Function of the two Ears in the Perception of Space.* By PROFESSOR SILVANUS P. THOMPSON, D.Sc., B.A.

1. **T**HE conceptions formed in our minds of the extension of space may be resolved into two parts:—(1) the conception of distance independent of direction; (2) the conception of direction independent of distance.

These conceptions are founded upon the perceptions of three separate senses, each of which, though distinct from the others, enables us to form conceptions both of linear magnitude (or distance) and of angular magnitude (or direction). These three senses are:—

- (a) The muscular sense;
- (b) The optical sense;
- (c) The auditory sense.

(a) The *muscular* sense gives us direct perceptions of linear magnitude and of angular magnitude through the sensations produced by extending the limbs and by twisting the frame and head.

(b) The *optical* sense gives us perceptions of angular direction of two kinds:—the first of them depending upon the optical formation of images of external objects upon the differentiated nerve-structures of the retina of the eye; the second of them being partly optical, partly muscular, and derived from the sense of muscular effort required to move the eye-balls, or the whole head, into the position in which light from an object situated in any given direction shall be most easily observed. The optical perception of distance is of three kinds—one kind being indirect and associative, the other two muscular. The *first* of these depends upon the possession of two eyes, giving, in consequence, two retinal pictures with slight differences, which we gradually learn to associate with varying conditions of distance. The *second*, and principal, of them depends also upon the possession of two eyes, the greater or lesser amount of muscular effort required to converge their optic axes in viewing an object affording a basis for a mental estimate of

\* Communicated by the Author, having been read before Section D of the British Association at York, September 1881.

distance. The *third* of them does not depend upon the possession of two eyes, or upon "binocular parallax," but consists in the perception by the muscular sense of the amount of effort which the ciliary muscle must exert to focus the eye for rays proceeding from an object at a given distance. The author has elsewhere \* shown how this last mode of perception is complicated by the question of the colour of the rays in consequence of the imperfect achromatization of the eye. To these three a fourth, and purely associative, kind of perception of distance must be added, in the apparent magnitude of objects of known size. Of these modes of perception, the two depending on binocular parallax are of greatest importance; without them our optical conceptions of solidity and distance would be extremely imperfect. The theory of binocular vision was practically complete when the invention of the stereoscope, and of its *reductio ad absurdum* the pseudoscope, proved the general correctness of Wheatstone's views, though several corollaries to the theory have since been elaborated by younger workers.

(c) The *auditory* sense may in like manner afford us perceptions of linear and of angular magnitude—that is to say, of distance and of direction. But the theory of the acoustical perception of space is strangely incomplete. Just as the possession of two eyes gives us by binocular parallax the most important of the optical means of perception of space, so the possession of two ears is found, from the researches of Mach, Luca, Steinhauser, Graham Bell, and of the present writer, to give us, by binaural parallax, important means for receiving acoustical perceptions of space. Besides these binaural perceptions, it is undeniable that imperfect monaural perceptions of space exist. These will be noticed in passing.

2. Any comparison of the *ear* and *eye* in respect of their power of affording perceptions of space would be incomplete if three points of essential difference in the arrangements of these organs were not adverted to:—

(i) The ear has no lens, and nothing equivalent to a lens by which a sound-wave proceeding in any given direction could be focussed on the receptive mechanism. The pinna or auricle of the ear and its auditory meatus do not even serve, as a hollow parabolic reflector might serve for light, to focus rays coming in different directions on different points of the receptive membrane.

(ii) The receptive nerve-structure of the ear is differentiated in a wholly different manner from that of the eye, so that its different parts are not sensitive to different *directions* in the

\* Phil. Mag. July 1877, [5] vol. iv. p. 48.



movement of acoustic waves, but only to their difference in frequency.

(iii) The ears cannot be turned toward different directions as the eyes can be, independently of the movements of the head, at least in man. There seems no reason, however, to doubt that the faculty of moving the pinnæ of the ears is useful to animals in their perception of the direction of a sound. It is a matter of common knowledge that horses, asses, cats, and dogs do thus use their pinnæ in ascertaining the direction of a sound. In these cases, however, it is doubtful whether there is any muscular sense of convergence to give (as with the eye) a perception of distance.

3. There are four physical characteristics of waves of sound by which one sound is discriminated from another, viz.:—

(i) *Intensity*, or loudness, depending upon extent or energy of the vibratory motions.

(ii) *Pitch*, or frequency, depending upon the rapidity of the vibratory motions.

(iii) *Phase* of the vibratory motions, as to whether moving backward or forward or at any other state.

(iv) *Quality*, or timbre, depending upon the degree of complexity of the vibratory motion.

The third of these physical characteristics is one for which the single ear possesses no direct means of perception. The author of this paper discovered in 1877\*, however, that in binaural audition a perception of difference of phase did exist; and the same discovery was made independently in the succeeding December by Prof. Graham Bell and Sir William Thomson. The existing theories of the acoustic perception of space, which will now be examined, are founded upon the perceptions of these four physical characteristics.

4. *Theories of Steinhauser and of Graham Bell.*—A very complete and careful theory of binaural audition was published in 1877 by Prof. Anton Steinhauser †, who worked out on geometrical principles the laws which determine the *relative intensity* with which a sound will reach the two ears when starting from any given point of space. The intensities are equal in the two ears when the source of sound is in the median plane, and is a maximum when in front, a minimum when behind the head, since the ears are set angularly (so as to catch sounds from the front of the head) in planes which determine, according to Steinhauser, the conditions of best hearing. The formula deduced by Steinhauser is the follow-

\* Rep. Brit. Assoc. 1877, p. 37; Phil. Mag. [5] vol. iv. Oct. 1877, p. 274.

† Vienna, 1877; Phil. Mag. [5] vol. vii. pp. 181, 261.

ing:—Let  $\beta$  be the angle between the plane of the ear and the line of sight, and  $\alpha$  the angle which the line of sight makes with the direction of the sound; and let  $i_1$  and  $i_2$  represent the relative intensity with which the sound is heard in the two ears; then

$$\tan \alpha : \tan \beta :: i_1 - i_2 : i_1 + i_2.$$

The operation, therefore, of finding the direction of a sound—say a lark singing high up in the air—will, according to Steinhauser, be as follows:—First, the head is rotated on its axis horizontally until the sound is equally loud in both ears; then the head is moved up and down until a maximum of loudness is discovered, when the lark will be found in the line of sight. Steinhauser's theory, it will be noted, takes into account no differences of phase, pitch, or quality, but of intensity only; and it fails, as will be seen, to account for the fact that we have, *without moving the head at all*, a very fair perception of the direction of sounds. It also presupposes (what the experiments of Crum Brown and M'Kendrick have pretty definitely shown to exist) that we possess a rotation-sense, a means of perception of angular movement in horizontal and meridional planes. Steinhauser devised an instrument, which he named the *homophone*, wherewith to test his theory. It consisted of a system of wooden tubes for bringing to the ears the sounds of two organ-pipes tuned to unison, whose respective intensities could be regulated by stopcocks. It was held by its inventor to confirm his theory.

A similar theory has been implicitly adopted by Prof. Graham Bell, in the paper on Experiments relating to Bin-aural Audition which he read before the American Association for the Advancement of Science in 1879\*. Graham Bell investigated the matter with telephones connected to the ears, with some curious and valuable results. He also experimented on the degree of accuracy with which the ear can determine the direction of a sound, and found it to be most accurately defined for those sounds the direction of which approximates to the axial line of the ears.

5. *Theories of A. M. Mayer and (provisionally) of S. P. Thompson.*—A modification of the preceding theory was provisionally adopted by the present writer in the earlier part of his researches. He had discovered that when two sounds agreeing in every respect, save in phase, are led to the ears, a singular phenomenon occurs, complete difference of phase producing an acoustical illusion as if the sound were localized in the back of the skull. He therefore suggested that differ-

\* American Journal of Otology, July 1880, p. 169.

ence of phase, being thus recognizable, might assist the observer in finding the true direction of a sound; for when his gaze was directed in the precise direction, not only would the relative intensities be equal, but the phase would be identical, and the sensation would be free from complication with the illusion.

Prof. Alfred M. Mayer of the Stevens Institute, in the course of his acoustic researches, suggested an instrument which he called the *topophone*, the object of which is to ascertain the direction of a source of sound, and which depends upon differences of phase and of intensity. An experiment of Zoch (see Radau, *Die Lehre vom Schall*, p. 246) for comparing the relative phases of two simple unison-tones by means of König's manometric flames, suggested to Mayer an instrument composed of two resonators fixed at the ends of a T-shaped frame, and connected with manometric flames, whose objective vibrations, as seen in a rotating mirror, would be synchronous when the phases and intensities of the sound-waves received in the two resonators were alike, or when the cross-arm on which they were fixed stood at right angles to the direction of the sound. In another form of the instrument, the frame carrying the resonators was fixed by a kind of yoke to the shoulders, the resonators being respectively connected by tubes to the two ears. Comparatively small angular movements of the head would then produce considerable differences of *phase*, rendering the perception of direction more narrowly accurate.

6. *Theories of Mach and of Lord Rayleigh*.—Prof. Mach, of Prague, advanced the theory (*Archiv für Ohrenheilkunde*, 1874) that the perception of direction of sound arose from the operation of the pinnae of the ears as resonators for the higher tones to be found in the compound sounds to which the ear is usually accustomed; their action as resonators should be more or less effective according to the position of the pinnae with respect to the direction of the sound-waves; and by thus reinforcing in different positions with unequal intensity, some one or more of the higher tones of a compound sound should affect the *quality* or timbre of the perceived sound, producing a difference between the sounds heard in the two ears in all positions, save when the source of sound lay in the median plane of the head. There should also, according to this theory, be a difference in the quality of the perceived sound (owing to the dissymmetry of the upper and lower parts of the pinna) for sounds in the median plane according as they were above, below, or in the line of sight. It will be convenient to consider along with the theory of Mach the somewhat similar theory of Lord Rayleigh\*, propounded in 1876 before the

\* Trans. Mus. Assoc. 1876.

Musical Association. Lord Rayleigh pointed out that, as the size of the head bears a finite proportion to the size of sound-waves, there will be no sharp shadows of sounds occurring at the opposite side of the head to that at which a sound arrives, but that *diffraction* of the sound-waves will take place, which, in the case of complex sounds, will produce the result that the partial tones of different pitch will arrive at the side of the head opposite to that nearest the source of sound with very different intensities. Thus, without making any assumption as to the functions of the pinnae as resonators, Lord Rayleigh's theory agrees with that of Mach in attributing the acoustic perception of direction to differences of *quality* or timbre between the two ears, the brain drawing, from the slight differences of the tones received in the two ears, an unconscious judgment based on empirical observation.

7. One other theory only will be mentioned, and this only to be at once dismissed. It is the theory advanced by Küpper \*, that sound-waves proceeding in different directions affect different parts of the tympanum, and so give rise to different sensations. This is physically untenable, because the tympanum is not the true receptive organ with differentiated nerve-structures, but only a part of a mechanical device by which the alternating compressions and rarefactions taking place at the bottom of the tube of the ear are conveyed to the true receptive organ in the labyrinth of the internal ear. It is also untenable because, as Mach and Fischer have shown, the outer ear cannot act as a true reflector except for waves whose length is a small fraction of its own dimensions, which is only true for sounds of such excessive shrillness as to be out of the range of ordinary sounds. [The shrillest sound audible in human ears is of wave-length 0·4 of an inch.] It is, finally, untenable because, in fact, nothing is more difficult than to tell the direction of sounds whose source is in the median plane of the head—front, back, zenith, and nadir being usually undistinguishable except for very well-known sounds.

8. In order to test the rival theories of binaural hearing, the author of this paper devised a little instrument, described before the British Association (Section A) in 1879 under the name of the *pseudophone* †, which is for the ears what Wheatstone's pseudoscope was for the eyes, an instrument for verifying the laws of perception by means of the illusions which it produces. The *pseudophone* consists merely of a pair of adjustable flaps or reflectors which can be fitted to the ears, and which can be set at any desired angle to catch sounds

\* *Archiv für Ohrenheilkunde*, n. F., Bd. ii, part 3, p. 158.

† *Phil. Mag.* [5.] vol. viii. 1879, p. 385.

from back, front, above, or below. By altering the position of the flaps, we alter the relative intensities of the two sounds as received in the ears; and this can be done without the blindfolded observer knowing how the flaps are set. If, for example, the flaps are set to catch sounds from behind, the observer will imagine that he is looking in the direction of the sound when he is looking in precisely the reverse direction. But when the *simple tones* of tuning-forks are used, the instrument fails to give satisfactory illusions, except for very shrill tones, when the experiments are made out of doors.

9. The following criticisms on the rival theories and on some of the results of mathematical and experimental deductions therefrom will now be in place.

(a) All the theories assume that we have a rotation-sense—that is to say, that when we turn round to face a sound, we are conscious how much (in angular measurement) we have turned round. Lord Rayleigh, in his experiments, kept the head still, and estimated the angular direction of the sound without turning the head. In this case association with previous perceptions of rotational movement must, however, be admitted as entering into the mental process of judging of angular position.

(b) The theory of Steinhauser leads to the mathematical deduction that perception of direction is the most exact for sounds situated in the *plane of best hearing*, or in the median plane and in front of the head. The experiments of Graham Bell, on the other hand, as well as those of Mach and of Lord Rayleigh, are conclusive that the perception of “the direction of a sound is more accurately defined as it approximates to the axial line of the ears.”

(c) Steinhauser's theory and his fundamental formula given above in § 4 assume that the ratio between the tangents of the angles will be the same in our perception as the ratio between the angles themselves. This is only true when both are small, and when therefore the source of sound is nearly in the median plane. Unfortunately for the theory, for very small angles the perception ceases to be accurate, especially for small angles near the median plane.

(d) Steinhauser's theory assumes the pinnae to act as reflectors and funnels; he further assumes the magnitude of the “effective surface” to be equal for sounds coming at all angles, which is by no means proven or even probable.

(e) It is a mathematical consequence of Steinhauser's theory, that if the plane of the effective surface of the pinna makes an angle of less than  $30^\circ$  with the line of sight, a sound will be heard louder when opposite one ear than when placed



at an equal distance in front of the head. With most people this angle is less; but most people, at any rate, prefer to face the source of sound when listening.

(*f*) It may be deduced from Steinhauser's theory that the perception of direction should be more accurately defined in those persons for whom the angle between the effective plane of the pinna and the line of sight is as small as possible. If this be so, persons whose ear-flaps stand off from their heads at a considerable angle should be bad judges of the direction of sounds, which is not, in general, the case. The behaviour of animals in bringing forward the openings of the pinnæ when listening intently to a sound is contrary to this point. If the deduction were true, women should be better judges of the direction of sounds than men, as their pinnæ usually are less prominent. In the experiments of Graham Bell with telephone-receivers when they were set at an angle with one another, he was able to perceive the direction of sounds more accurately than when the receivers were set parallel, the difference between back and front being thus capable of discrimination; but he does not state whether this discrimination arose merely from difference in relative intensity or from difference of quality.

(*g*) If the theory of Steinhauser is true, the perception of direction should be more accurate for sounds when their source is far away than when it is near the head. If the theory of Lord Rayleigh and of Mach is true, the perception of direction should be more accurate for sounds whose source is nearer the head. The latter is shown by experiment to be true for all kinds of sounds.

(*h*) The theory of Lord Rayleigh is supported by the experimental fact that the quality of sounds does, as a matter of fact, differ when they are heard in different directions. Compare, for example, the sound of a musically ticking clock placed in front of the head with the sound of the same clock when the head is turned in the opposite direction. To the writer the tick of a watch always sounds deeper in pitch when held in front of the head than when held opposite either ear, in each case at equal distances of about one foot away.

(*i*) The theory of Lord Rayleigh also derives support from the following observation. To analyze a compound sound by ear, so as to say what partial tones are present, requires considerable practice, and is even then not easy. But the presence or absence of partial tones is rendered much easier of detection if the head be turned about, so that their various degrees of intensity as affected by diffraction or by phase-difference may bring one or other into prominence.

(j) The theories of Mach and Lord Rayleigh agree with that of Steinhauser in one respect. They assign, it is true, the perception of direction of a sound to the effect of resonance or of diffraction in partially resolving a compound tone; but they make the perception of this splitting-up of the sound to depend upon the *unequal intensity* with which the resolved sounds are received in the two ears.

(k) The experiments of Lord Rayleigh show that our perception of direction is much more accurate for compound sounds than for simple tones.

(l) The experiments of the writer with the pseudophone show that the acoustic illusions are produced much the most satisfactorily when shrill sounds, such as the sound of a whistle or the click of a metronome, are employed.

(m) Experiments made with very low tones show that for these the sense of direction is extremely inaccurate. In this case the extreme effect of diffraction would cause the sound to be heard almost equally loudly by both ears in all positions.

10. It would therefore appear that Steinbauser's theory may be true for shrill and simple tones, and therefore true for the particular case of the lark. But for baser tones and for compound tones it cannot be regarded as true. For these the resolution-theories of Mach and Lord Rayleigh are much more nearly in accord with the facts of observation; though it probably yet remains to be determined whether the resolution of compound tones supposed in those theories be due, as Lord Rayleigh assumes, to diffraction round the head, or, as Mach assumes, to the pinna and its convolutions acting as resonating-cavities to reinforce certain of the partial tones of the compound sound. The former is the more probable in the opinion of the present writer; but it is not without its difficulties.

If in binaural hearing the direction of sound were to be estimated only by the process of moving the head until the line of sight coincided with that of the sound, then Steinhauser's theory accounts best for the facts.

If, however, the direction be estimated while the head is held immovable, then the resolution theories are certainly the more satisfactory.

In view of the fact (as apparently shown by Graham Bell's experiments) that even in *monaural audition* there is a fair perception of the direction of sound, Steinhauser's theory utterly fails to have any significance; while the theories of Mach and of Lord Rayleigh are amply sufficient for the facts.

11. The writer therefore propounds the following theory, which he believes to cover all the facts observed up to the present time.

*Judgments as to the direction of sounds are based, in general, upon the sensations of different intensity in the two ears; but the perceived difference of intensity upon which a judgment is based is not usually the difference in intensity of the lowest or fundamental tone of the compound sound (or "clang"), but upon the difference in intensity of the individual tone or tones of the clang for which the intensity-difference has the greatest effective result on the quality of the sound.*

It must be admitted that the acoustical perception of direction is, after all, not intuitive, but associative, just as the optical perception of direction is. The ear has been trained from childhood to associate certain differences in the quality of sounds (arising from differences in the relative intensities of some of the partial tones that may be present) with definite directions; and, relying on these associated experiences, judgments are drawn concerning sensations of sound whose direction is otherwise unknown. For sounds that are familiar a difference of quality as heard in one ear will at once suggest a direction. It is completely open to doubt whether a pure simple tone heard in one ear could suggest any direction at all.

12. *Acoustical Perception of Distance.*—There remains for discussion the acoustical perception of distance.

In the case of known sounds we doubtless judge chiefly of their distance by their relative loudness, the intensity decreasing inversely as the square of the distance. The analogous fact in optics is the perception of distance by the apparent magnitude of objects familiar to the sight and of known size.

It might be possible indirectly, in the case of short distances, to judge of distance by "acoustic parallax"—that is to say, by the difference in the direction of the sound as perceived in the two ears. The quality of a compound sound also differs slightly with distance (independently of direction); and from this fact a judgment might be drawn. It must be held extremely doubtful, however, whether any such judgments are actually made.

13. *Conclusion.*—The foregoing arguments and deductions have been based upon observations made, so far as the author is aware, exclusively by and upon persons possessed of normal powers of hearing. Nevertheless the subject is of such a nature that its more obscure points would doubtless be greatly

elucidated by observations made by and upon persons whose hearing-power is abnormal. The author has had no opportunities of making such observations. He has heard of one case of interest—that of a gentleman stone-deaf of one ear from infancy, and in whom the acoustic perception of direction was almost wholly wanting. Not only are experiments greatly wanted upon semi-deaf persons, but also upon blind persons, who usually have the acoustic perception of direction abnormally acute. It would be still more desirable to have observations made on a blind person deaf of one ear.

It is also greatly to be desired that further experiments should be made to determine the exact function of the *pinnæ* and of their complicated forms. The convolutions of the *pinnæ* differ markedly in different persons, and such differences must have *some* effect on the perception of sound. The suggestion of Mach, that the convolutions have no direct acoustic function in man, but that they represent the corresponding structures which in animals serve to direct the opening of the *pinnæ* or to prevent them from being turned inside out, is probably true, and is in conformity with the doctrine of descent, which accounts for many other inherited but functionless appendages. Yet, if true, this does not affect the truth of the statement that the convolutions, though destitute of direct function, must still exercise some effect on the perception of sound. In particular, it may be remarked that the outer cartilaginous rim of the ear curves forward at the upper part of the pinna, as if to catch sounds proceeding from below the observer and in front of him. Is it possible that this arises by natural selection from the fact that, on level ground, sounds reach us more intensely from below, by reflexion from the ground? And is it not also connected with the fact that persons who are partially deaf in both ears habitually throw the head a little backward, so as to raise their line of sight above the direction of the sound of the speaker's voice?

Whether the varieties of form of the *pinnæ* eventually prove to be of little or no importance in the question, there is an ample field for observation for anatomists and physiologists in the problems of the acoustical perception of space; and it is hoped that research in this department of physiological physics will be facilitated by the attempt now made to lay down the physical and experimental bearings of the question.

LII. *A Theorem on the Dissipation of Energy.*

By S. H. BURBURY\*.

I THINK the following theorem has never received a formal proof.

A material system being in motion, and there being dissipation of energy by friction or otherwise, external forces,  $F$ , are applied to maintain certain of the velocities constant. If under these circumstances the system ultimately acquires a motion in which it might move were there no dissipation and no external forces, then in such motion the energy dissipated per unit of time is minimum, given the constant velocities.

For let  $q_1, q_2, \dots q_n$  be the generalized coordinates defining the position of the system;  $\dot{q}_1, \dot{q}_2, \dots \dot{q}_n$  the corresponding velocities;  $p_1, p_2, \dots p_n$  the corresponding generalized components of momentum.

Let  $\dot{q}_1, \dot{q}_2, \dots \dot{q}_r$  be the velocities which are maintained constant by the application of the forces  $F$ .

Then we have for each coordinate, by Lagrange's equations,

$$\frac{dp}{dt} - \frac{dT}{dq} + \frac{dU}{dq} = F_q - \frac{dH}{d\dot{q}},$$

where  $T$  is the kinetic,  $U$  the potential energy,  $F_q$  is the generalized component of the external forces corresponding to  $q$ , and  $H$  is Lord Rayleigh's dissipation function, namely the energy dissipated per unit of time. The ultimate motion is by hypothesis one in which the system might move were there no dissipation and no forces  $F$ . That is ultimately, by hypothesis,

$$\frac{dp}{dt} - \frac{dT}{dq} + \frac{dU}{dq} = 0,$$

and

$$F_q = \frac{dH}{d\dot{q}}$$

for each coordinate.

Now let us suppose that in the infinitely small time  $dt$ , the given velocities  $\dot{q}_1 \dots \dot{q}_r$  would be diminished by dissipation alone by the quantities  $\dot{q}'_1 \dots \dot{q}'_r$ . Then, in order to maintain them constant, the forces  $F$  must in that same time  $dt$  produce in the system the velocities  $\dot{q}'_1 \dots \dot{q}'_r$ . We may suppose the forces  $Fdt$  applied impulsively at the end of the interval of time  $dt$  to produce the velocities  $\dot{q}'_1 \dots \dot{q}'_r$ .

Now a set of impulses applied to produce in the system the prescribed velocities  $\dot{q}'_1 \dots \dot{q}'_r$  will generally produce at the same time other velocities  $\dot{q}'_{r+1} \dots \dot{q}'_n$ , the whole impulsive motion being, according to Thomson's theorem, determined

\* Communicated by the Author.



by the condition that the kinetic energy of the system moving with these velocities  $\dot{q}'_1 \dots \dot{q}'_r \dots \dot{q}'_n$ , and no others, is minimum, given  $\dot{q}'_1 \dots \dot{q}'_r$ . That is, if  $p'_1 \dots p'_n$  be the components of momentum corresponding to  $\dot{q}'_1 \dots \dot{q}'_n$ ,  $\Sigma p' \dot{q}'$  is minimum, given  $\dot{q}'_1 \dots \dot{q}'_r$ . The solution of which is

$$p'_{r+1} = 0 \dots p'_n = 0.$$

But  $p'_1 \dots p'_n$  being the components of momentum produced impulsively by the force  $F dt$ , each component of momentum is equal to the corresponding component of force. That is, for each coordinate

$$p' = F_q dt.$$

But, as we have seen,

$$F_q = \frac{dH}{d\dot{q}};$$

therefore

$$p' = \frac{dH}{d\dot{q}} dt.$$

Therefore, since  $p'_{r+1} = 0$  &c.,  $p'_n = 0$ ,

$$\frac{dH}{d\dot{q}_{r+1}} = 0 \dots \frac{dH}{d\dot{q}_n} = 0.$$

And therefore  $H$  is minimum, given  $\dot{q}_1 \dots \dot{q}_r$ .

As an example of the theorem we may consider the distribution of an electric current in multiple arc. Let a set of wires,  $OC_1P$ ,  $OC_2P$ , ...  $OC_nP$ , be joined at  $O$  and  $P$ , and a constant current be maintained outside the junction at  $O$ . Let  $\dot{q}_1 \dots \dot{q}_n$  denote the currents in the several wires,  $p_1 \dots p_n$  the corresponding components of electrokinetic momentum. Then the current at  $O$  is  $\Sigma \dot{q}$ , and is to be maintained constant notwithstanding the resistance of the wires.

Let  $\dot{q}'_1 \dots \dot{q}'_n$  be the diminutions of the several currents which would be caused by resistance in the infinitely small time  $dt$ . Then  $\Sigma \dot{q}'$  is the diminution of the current at  $O$  due to resistance in time  $dt$ . In order to maintain  $\Sigma \dot{q}$  constant, we may suppose an impulsive electromotive force applied at  $O$  at the end of the interval  $dt$  to produce the current  $\Sigma \dot{q}'$ .

The distribution among the wires of this current  $\Sigma \dot{q}'$ , at the instant of its creation, for however short a time such distribution may continue, is determined by the laws of induction, and will, by Thomson's theorem, be such as to make the electrokinetic energy of the impulsive currents minimum, given  $\Sigma \dot{q}'$ . That is, if  $p'$  be the component of electrokinetic momentum corresponding to  $\dot{q}'$ ,  $\Sigma p' \dot{q}'$  is minimum, given  $\Sigma \dot{q}'$ . That is,

$$p'_1 = p'_2 = \dots = p'_n.$$

But if  $E$  be the component of electromotive force correspond-

ing to any wire,

$$Edt = p',$$

and therefore

$$E_1 = E_2 = \dots = E_n.$$

Now for each wire

$$\frac{dp}{dt} = E - R\dot{q},$$

where  $R$  is the resistance in the wire. Ultimately, when the motion becomes steady, which it does generally in a very short time,

$$\frac{dp}{dt} = 0,$$

and therefore

$$E = R\dot{q}.$$

But

$$E_1 = E_2 = \dots = E_n;$$

therefore

$$R_1\dot{q}_1 = R_2\dot{q}_2 = \dots = R_n\dot{q}_n;$$

and therefore  $\Sigma R\dot{q}^2$ , or the heat generated in the wires per unit of time, is minimum, given  $\Sigma\dot{q}$ .

This is the distribution according to Ohm's law, which thus appears as an analytical consequence of Thomson's theorem.

### LIII. On Retardation of Chemical Action.

By JOHN J. HOOD, B.Sc., Assoc. R.S.M.\*

IN two former papers published in this Journal† I have given the results of a series of experiments on the rate of oxidation of ferrous sulphate by potassic chlorate, and showed that the course of the reaction for equivalent quantities of the substances is represented by the equation  $y(a+t) = b$ ; the variables being the amount of unoxidized iron expressed in cubic centimetres of a solution of potassic permanganate, and time elapsed from a fixed point in the reaction. This equation is established on the supposition that the products formed have no influence on the rate at which the oxidation goes on; but when an experiment was continued for a comparatively long period, or till about 80 per cent. and upwards of the oxidation had taken place, a small and ever increasing difference was apparent between the calculated and observed variables, indicating a retardation which was due, without doubt, to the products of the reaction.

The present paper contains the results of a series of experiments made to investigate this retarding effect, in a general

\* Communicated by the Author.

† Phil. Mag. [5] vi. p. 371; viii. p. 121.

way, by employing such salts as could not influence the oxidation of the iron by any process of double decomposition.

A solution (about 8 litres) of ferrous sulphate and hydric sulphate was prepared from pure materials and preserved in a large glass jar, arranged in such a way that any required quantity of the solution could be siphoned off, while an atmosphere of coal-gas was always maintained inside the jar. This solution contained in 100 cubic centim.

3.1416 grams ferrous iron,  
 .038 gram ferric iron,  
 11.84 grams free hydric sulphate.

The solution of potassic chlorate contained in 100 cubic centim. 1.933 gram. 10 cubic centim. being the amount required to oxidize the iron in 16.86 cubic centim. of the ferrous sulphate solution. The method of performing the experiments was the same as has been already described in my former papers.

Each experimental solution consisted of 16.86 cubic centim. of the iron solution or .5296 gram  $\text{Fe}''$ , and 1.996 gram free  $\text{H}_2\text{SO}_4$ , together with the requisite amount of the salt whose retarding effect was to be determined, the total volume being made up to 250 cubic centim. with distilled water.

The salts employed were purified from all traces of iron and chlorides, dissolved in distilled water, and the strengths of the solutions determined by double estimations of base and acid.

The flasks containing the experimental solutions were placed in a water-bath, usually six at one time, 10 cubic centim. of the chlorate solution run into each, and the amount of oxidation that had taken place after the lapse of various intervals of time determined by permanganate. From two observations of the amount of unoxidized iron and time, the constants in the equation  $y(a+t)=b$  were calculated, three minutes after the addition of the chlorate being taken in every case as the point  $t=0$ .

As  $b$  in the above equation is inversely proportional to the rate of change, or

$$\frac{dy}{dt} = -\frac{y^2}{b},$$

by a comparison of its values for a series of experiments, in which other conditions being the same except the amount or kind of salt added, with its value for a blank experiment, or that in which no retarding agent is present, a measure of the effect is obtained; these ratios multiplied by 100 are given in Table II.

To determine the equation for the blank as accurately as possible, twenty-four experiments were made, in four batches

of six each, at various times during the course of the work, which lasted about two weeks, the first batch at the commencement and the fourth at the finish. The mean values obtained were:—

<i>a.</i>	<i>b.</i>	} temp. 21° C.,
113·8	1113·8	
112·9	1112·5	
112·4	1110·8	
113·0	1115·7	
Means . . 113·02	1113·2	

or the equation for the blank experiment,

$$y(113\cdot02 + t) = 1113\cdot2.$$

The following Table contains the mean values for these same constants from two and, in some cases, four experiments, and the weight (calculated as anhydrous) of the various salts present in each:—

TABLE I. Temp. 21° C.

Weight of salt.	K <sub>2</sub> SO <sub>4</sub> .		Na <sub>2</sub> SO <sub>4</sub> .		(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .	
	<i>a.</i>	<i>b.</i>	<i>a.</i>	<i>b.</i>	<i>a.</i>	<i>b.</i>
2 grams...	134·5	1340	134·8	1343	134·3	1345
3 " ...	145·5	1456	146·5	1464	147	1473·7
4 " ...	159·6	1592·7	159·5	1595·5	161·5	1618·4
5 " ...	170·5	1708	167·7	1691	171·2	1725
6 " ...	185·3	1860·4	184·3	1853·7	184·9	1850
8 " ...	214	2180·5	210·8	2120·3	212	2150·7
10 " ...	243·1	2468·6	233·5	2365	235	2381·3

Weight of salt.	KAl(SO <sub>4</sub> ) <sub>2</sub> .		(NH <sub>4</sub> )Al(SO <sub>4</sub> ) <sub>2</sub> .	
	<i>a.</i>	<i>b.</i>	<i>a.</i>	<i>b.</i>
2 grams...	126·6	1249·3	127·8	1244
3 " ...	133·3	1315·4	133·4	1316·6
4 " ...	140·6	1387·6	139·7	1384·5
5 " ...	144·8	1442·5	145·5	1444·5
6 " ...	154·7	1537·5	154	1529·4
8 " ...	163·7	1627·8	160·9	1608·8
10 " ...	173·4	1727·5	171·7	1704·5

Weight of salt.	MgSO <sub>4</sub> .		ZnSO <sub>4</sub> .	
	<i>a.</i>	<i>b.</i>	<i>a.</i>	<i>b.</i>
2 grams...	128·5	1278·5	123·8	1225·6
3 " ...	139·1	1375·4	129·8	1280·3
4 " ...	144	1429·5	131·5	1308
5 " ...	149·5	1492·2	138	1369·5
6 " ...	156	1569·4	141·6	1414·3
8 " ...	168	1680·1	147	1477
10 " ...	179·2	1793·5	155	1540·3

Taking the value of  $b$ , or 1113·2, for the blank experiment as equal to 100, and expressing the corresponding values of this quantity contained in the above Table in terms of it, the numbers contained in the following Table are obtained; they, in point of fact, represent the number of minutes required to oxidize the iron in each solution from  $y'$  to  $y''$ , the time required to perform the same amount of oxidation in the blank experiment being 100 minutes.

TABLE II.

Weight of salt.	$K_2SO_4$ .		$Na_2SO_4$ .		$(NH_4)_2SO_4$ .	
	$\frac{100b'}{b}$ .	Retardation for 1 gram.	$\frac{100b'}{b}$ .	Retardation for 1 gram.	$\frac{100b'}{b}$ .	Retardation for 1 gram.
2 grams ...	120·3	10·1	120·6	10·3	120·8	10·4
3 " ...	130·8	10·2	131·5	10·5	132·4	10·8
4 " ...	143·1	10·8	143·3	10·8	145·3	11·3
5 " ...	153·4	10·7	151·9	10·4	154·9	10·9
6 " ...	167·1	11·2	166·5	11·1	166·2	11·0
8 " ...	195·8	11·9	190·5	11·3	193·2	11·6
10 " ...	221·7	12·2	212·4	11·2	213·9	11·4

Weight of salt.	$KAl(SO_4)_2$ .		$(NH_4)Al(SO_4)_2$ .	
	$\frac{100b'}{b}$ .	Retardation for 1 gram.	$\frac{100b'}{b}$ .	Retardation for 1 gram.
2 grams ...	112·2	6·1	111·8	5·9
3 " ...	118·1	6·0	118·3	6·1
4 " ...	124·7	6·2	124·4	6·1
5 " ...	129·6	5·9	129·7	5·9
6 " ...	138·1	6·3	137·4	6·2
8 " ...	146·2	5·8	144·5	5·6
10 " ...	155·2	5·5	153·1	5·3

Weight of salt.	$MgSO_4$ .		$ZnSO_4$ .	
	$\frac{100b'}{b}$ .	Retardation for 1 gram.	$\frac{100b'}{b}$ .	Retardation for 1 gram.
2 grams ...	114·9	7·4	110·1	5·0
3 " ...	123·6	7·8	115	5·0
4 " ...	128·4	7·1	117·5	4·4
5 " ...	134	6·8	123	4·6
6 " ...	140·9	6·8	127	4·5
8 " ...	150·9	6·4	132·7	4·1
10 " ...	161·1	6·1	138·4	3·8

From the numbers contained in Table II., it will be seen that the retardation in the rate of oxidation of ferrous sulphate



by potassic chlorate is proportional to the weight of the chemically inactive salt present, and that the amount of this retardation is the same for equal weights of those salts which more or less resemble each other constitutionally. This is seen to hold for the sulphates of the alkaline metals and ammonium, and also for the two alums; but in the case of the sulphates of zinc and magnesium the difference in their effects is too considerable to permit of their being classed together, in a dynamical sense, however much they may resemble each other statically. The fact that equal weights of the alkaline sulphates or the alums produce equal effects, shows that the retardation produced by a single molecule of those salts which belong to the same group is proportional to its weight.

Mills and Walton have shown\* that, in the formation of ammonia by the action of zinc amalgam on potassic nitrate, the presence of sodic or potassic sulphate produces an acceleration in the reaction, and that equal weights of the two salts have, as nearly as possible, equal working effects.

My best thanks are due to Dr. Frankland, in whose laboratory the above experiments were made.

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LIV. *Note on the supposed Helical Path of the Electric Current in longitudinally Magnetized Conductors.* By J. A. EWING, B.Sc., F.R.S.E., Professor of Mechanical Engineering in the University of Tokio, Japan†.

IN a paper entitled "Molecular Magnetism," read before the Royal Society on May 19, Prof. Hughes describes experiments which have led him to the conclusion "that the path of an electric current through an iron or steel wire is that of a spiral." Prof. Hughes mentions that the wires experimented on were never entirely free from longitudinal magnetization to begin with, and that when they were further magnetized the effects observed, which formed the ground of the conclusion just quoted, were greatly increased. It may fairly be assumed that these effects were in all cases due to the presence of longitudinal magnetism in the wires.

The object of this note is to point out that the experimental results obtained by Prof. Hughes admit of another interpretation than that which he has given them, and at the same time to suggest a method of determining whether there is, or is not, any such helical quality in the path of the current as he has inferred.

\* Proc. Roy. Soc. 1879.

† Communicated by the Author.

In Prof. Hughes's experiments, magnetized iron or steel wire was placed inside and along the axis of a coil which was in circuit with a telephone. The coil could be turned about an axis perpendicular to the wire. By means of the telephone it was observed that, even when the wire was normal to the plane of the coil, a series of currents were induced in the coil when an intermittent current was made to pass along the wire. By turning the plane of the coil round through a certain angle, silence was restored in the telephone. This result would, of course, be consistent with the hypothesis that the path of the current in the wire is not rectilinear but helical.

But it is clear that the same inductive effects would be given by changes in the longitudinal magnetization of the wire accompanying the changes in the transmitted current.

Weber's theory of magnetization, which assumes that the molecules of iron or steel are always magnets, and that magnetization consists in bringing their axes into more or less complete parallelism, implies that if magnetization exists in one direction, then any supplementary magnetization at right angles to that must produce a diminution of the first. The degree to which the second magnetization affects the first will depend on the nearness of the latter to its limiting value. If it approaches that closely, then the second magnetization will take place wholly at the expense of the first. Hence, when a current traverses a longitudinally magnetized wire, the circular magnetization caused by the current must reduce the original longitudinal magnetization. The first passage of the current will produce a relatively large effect; and subsequent interruptions and renewals of it will cause fluctuations in the value of the magnetic moment, whose external inductions will be precisely the same as if the path of the traversing current were a helix.

The experiments of Prof. Hughes agree with this deduction from Weber's theory. A current entering at the nominal N. pole gave an inductive effect corresponding to a right-handed spiral; entering at the S. pole, it gave an effect corresponding to a left-handed spiral. Hence the inductions were in both cases of the kind which would be produced by a diminution of the original magnetization of the wire.

A second experiment consisted in passing a steady current through the wire from N. to S., and superposing on it an intermittent current. The inductive effects were then such as would correspond to a right-handed spiral, both when the direction of the intermittent current was the same as that of the steady one and when their directions were opposite. From

the point of view now suggested we have, in the first case, a further diminution of longitudinal magnetization by the intermittent current, and in the second case a partial restoration of it; and these changes would account for the observed facts. An examination of Prof. Hughes's paper will show that his other experiments bearing on this point admit equally well of the same explanation.

On the other hand, we have a reason for anticipating that the path of the electric current in a magnetized wire will be found to possess some helical quality.

The circular magnetization due to the current, together with the existing longitudinal magnetization, gives a helical magnetization which will be right-handed (like a common screw) when the current enters at the S. pole. It is known that magnetization develops an æolotropic difference of electrical conductivity along and across the lines of force. If then the conductivity be greater across than along the direction of magnetization, the path of a current entering at the S. pole will be a left-handed helix. The inductive effects will in that case be of the same sign as those observed by Prof. Hughes.

Sir William Thomson (Phil. Trans. 1856, part 3) has concluded that in iron the effect of magnetism on conductivity is to give greater resistance along than across the lines of induction. This would give a helical quality of the kind supposed by Prof. Hughes; but the difference in conductivities is so small as to make it highly improbable that this action accounts for the very considerable inductions observed by him. In steel the effect is more doubtful (*cf.* Thomson, *loc. cit.*; Tomlinson, Proc. Roy. Soc. June 17, 1875; F. Auerbach, Phil. Mag. 1879, Nos. 46-48).

These considerations indicate that the induced currents in the coil are, probably, due in chief part to changes of longitudinal magnetization which accompany the passage and stoppage of the current in the wire; also that there may be some effect caused directly by the solenoidal component of helical currents, whose helical path is attributable to the development of a difference of conductivities by helical magnetization. Further, it is obvious that if (from this or any other cause) there is a solenoidal quality in the path of the current, the change of magnetic moment and the induced currents will be indirectly increased by the magnetizing action of this solenoid on those parts of the metal which may be considered to lie within it.

The method used by Prof. Hughes does not enable us to distinguish between the part of the action due to change of

longitudinal magnetization, and the part (if any) due to a solenoidal component of the current. The same remark applies with equal force to any observation of the induction *outside* the magnetized conductor.

But if we use a hollow iron or steel rod in place of a solid wire, and test the magnetic force inside it, we may at once determine whether any part of the observed effect is due to a circulation of the current round the rod. Let the rod be long compared with its transverse dimensions, and let it be uniformly magnetized. In the first instance, the magnetic force at the middle of its length, either inside or outside, due to its longitudinal magnetization, is

$$-\frac{M}{a^3},$$

where  $M$  is its magnetic moment and  $a$  its half length. When a current is passed along the rod there will be (by Prof. Hughes's experiment) a diminution of its moment. Let this diminution of moment be  $\Delta M$ . Then outside the rod, at the centre, the magnetic force will be changed by the amount

$$\frac{\Delta M}{a^3}.$$

But inside, if any part of the effect is due to a solenoidal arrangement of the current, an electromagnetic force will be produced equal to

$$-4\pi Cn,$$

where  $C$  is the current, and  $n$  the number of turns in this solenoid per unit of length. The actual change of force at an internal point midway between the ends will therefore be

$$\frac{\Delta M}{a^3} - 4\pi Cn.$$

The question whether the second term of this expression has any sensible existence, is to be answered by observing the change of force inside when the current is made, and at the same time observing the change of moment of the rod, or by making simultaneous or successive measurements of the force outside and inside.

Various ways of carrying out this experiment will suggest themselves. The two following plans, which I hope soon to put to the test, appear practicable; the second, in particular, seems capable of a high degree of delicacy.

I. Suspend inside the hollow rod a magnet of known moment, and small enough to leave some clearance for swinging. Time the oscillations of this magnet both before and

during the passage of the current, and observe the loss of moment ( $\Delta M$ ) of the hollow rod. See whether the change of magnetic force deduced from the oscillations is or is not less than  $\frac{\Delta M}{a^3}$ .

II. Prepare two small coils of precisely equal inductive power. Place one inside, and the other outside, the hollow rod at the middle of its length. Connect them both to a ballistic galvanometer or a telephone in such a manner that, if the currents induced in them are equal, there will be no resultant effect. Then pass a current along the rod. If the effects are simply magnetic, the induction will be the same for both coils; but if the passage of the current produces any electromagnetic force in the interior, this equilibrium will be much disturbed.

This last has the merit of being a null method; and it has the additional advantage, that a strong longitudinal magnetization may be given to the rod by enclosing it in a long solenoid through which a steady current may be kept circulating during the experiment.

Tokio, Japan,  
September 22, 1881.

LV. *On the Dimensions of a Magnetic Pole in the Electrostatic System of Units.* By J. J. THOMSON.

*To the Editors of the Philosophical Magazine and Journal.*

Trinity College, Cambridge,  
May 16, 1882.

GENTLEMEN,

IN the last number of the *Philosophical Magazine* there is a paper by Prof. J. D. Everett, on the Dimensions of a Magnetic Pole in the Electrostatic System of Units, in which he supports the view taken by Clausius, that in this system the dimensions of a magnetic pole are  $M^{\frac{1}{2}}L^{\frac{3}{2}}T^{-2}$ , and not  $M^{\frac{1}{2}}L^{\frac{1}{2}}$  as stated by Maxwell. Clausius gets his value from the equation

$$\text{Moment of magnet} = \text{current} \times \text{area}.$$

It seems to me, however, that the equation should be

$$\text{Moment of magnet} = \mu \text{ current} \times \text{area};$$

where  $\mu$  is the magnetic permeability of the medium in which the current is placed, and is of dimensions  $T^2L^{-2}$  in the electrostatic system: if we use this equation we get the same dimensions for the magnetic pole as Maxwell. The following are the reasons which seem to me to show that the value given by Maxwell is the correct one. It will be convenient to see how Maxwell's value is obtained. The easiest way of getting



it is to deduce it from the expression given by Maxwell for the magnetic force produced by an electric current. Maxwell, in his 'Electricity and Magnetism,' 2nd edit. §§ 498, 499, makes the following statements about the magnetic force due to a current:—

"If any closed curve be drawn and the line-integral of magnetic force taken completely round it, then if the closed curve be not linked with the circuit the line-integral is zero; but if it is linked with the circuit so that the current  $i$  flows through the closed curve, the line-integral is  $4\pi i$ . The line-integral  $4\pi i$  depends solely on the quantity of current and not on any other thing whatever. It does not depend on the conductor through which the current is passing. Again, the line-integral  $4\pi i$  does not depend on the medium in which the closed curve is drawn. It is the same whether the closed curve is drawn entirely through air, or passes through a magnet or soft iron, or any other substance whether paramagnetic or diamagnetic."

Hence, if  $F$  be the magnetic force due to an infinitely long straight current of strength  $i$  at a distance  $r$  from the current, it may without any ambiguity be written

$$F = \frac{2i}{r}.$$

Now the work done when a magnetic pole of strength  $m$  is carried round the current so as to remain at a constant distance  $r$  from it, is  $mF2\pi r$ , or, by the above equation,  $4\pi mi$ . Hence the product  $mi$  is of the dimension of energy; but on the electrostatic system  $i$  is of the dimension  $M^{\frac{1}{2}}L^{\frac{1}{2}}T^{-2}$ : hence  $m$  must be of dimension  $M^{\frac{1}{2}}L^{\frac{1}{2}}$ , the value given by Maxwell.

The dimensions of  $F$  the magnetic force are  $M^{\frac{1}{2}}L^{\frac{1}{2}}T^{-2}$ , the magnetic induction  $m/r^2$  is of dimension  $M^{\frac{1}{2}}L^{-\frac{3}{2}}$ ; hence the magnetic permeability  $\mu$ , which is the ratio of magnetic induction to magnetic force, is of dimensions  $L^{-2}T^2$ .

If  $R$  be the magnetic force due to a pole of strength  $m$  at a distance  $r$  from it, the magnetic induction is  $\mu R$ . Now the magnetic induction integrated over any surface containing the pole and no other magnetic matter  $= 4\pi m$ . Hence, taking the induction across the surface of a sphere whose centre is the pole and radius  $r$ , we get

$$\mu \cdot R \cdot 4\pi r^2 = 4\pi m;$$

$$\therefore R = \frac{m}{\mu r^2}.$$

Hence the force between two poles  $m, m'$  is  $mm'/\mu r^2$ . Thus the force between two magnetic poles depends on the medium in

which they are placed ; but, according to Maxwell, the magnetic force between a current and a magnetic pole does not. Hence the moment of the magnetic shell equivalent to a given current depends on the medium surrounding the shell. If the field be occupied by one medium only, the moment of the magnetic shell  $= \mu \cdot \text{current} \times \text{area}$ . This equation gives the dimensions  $M^{\frac{1}{2}} L^{\frac{1}{2}}$  for  $m$ .

The effect of the medium surrounding a current upon the magnetic force produced by the current has, as far as I know, not been investigated. The only experiments I know bearing on this point are some experiments of Faraday on the effect of the surrounding medium on the electric currents induced by a moving magnet. The result of the experiments was, that he could not detect that changing the medium had any effect on the induced currents. If this be so, then Maxwell's statement must be right. For, imagine a long magnet in presence of an electric current, and let one pole be in one medium and the other in another ; then, if the forces on the two poles are different in magnitude, we may carry the magnet round the current so as to get work out of it. Now this work must have come from the battery ; but, since the inductive action of the magnet on the current is independent of the medium, there will be on the whole no currents induced by the motion of the magnet : hence no work can come from the battery ; hence the forces on the poles must be equal, or the magnetic force produced by a current must be independent of the surrounding medium. I may mention that Mr. E. B. Sargent, of Trinity College, is at present experimentally investigating this point. Mr. W. D. Niven has pointed out to me that the value given by Clausius for the dimensions of a magnetic pole does not make the magnetic force between two such poles of the dimensions of a force, which ought clearly to be the case.

I am, Gentlemen,

Your obedient servant,

J. J. THOMSON.

LVI. *On the Electrostatic Dimensions of a Magnetic Pole.*

By Prof. J. LARMOR\*.

CLAUSIUS'S formula to connect the dimensions of current and pole on the static system, viz.

(A) Moment of Magnet = Current  $\times$  Area,

seems really to involve the electromagnetic system of units. It is plain that, to be able to make and establish *practically*

\* Communicated by the Author.

such a relation as to the magnetic action of a current, we must assume tacitly these previous relations (which in fact supply our only mode of comparison and verification), viz.:—

$$(1) \quad (\text{Pole})^2 \times L^{-2} = \text{Force},$$

$$(2) \quad \text{Current} \times L \times \text{Pole} \times L^{-2} = \text{Force}.$$

The first of these is the purely magnetic starting-point of the electromagnetic system; and the second is the relation which must be used to connect current with pole *on any system*. But the electrostatic system naturally starts with the dimensions of electric quantity as deduced from the law of inverse squares, whence those of current are deduced at once. Now, the only simple fact of nature which connects pole with current is Oersted's phenomenon (as developed by Ampère) of the existence of a mutual force between them: this is expressed by (2); and hence by this relation must we deduce the dimensions of pole from those of current already found. The somewhat recondite fact that the magnetic action of a small circuit carrying a current may be represented as due to two *fictional* magnetic poles, does not seem to possess any claims to supplant the natural statement of the only fundamental relation which makes *natural* poles play a part in electric theory at all. That relation is, of course, itself in its very nature electromagnetic.

It might be said that the system objected to built up the theory from electric foundations, inasmuch as its fundamental magnet is a small electric current. But, in reply, it is the existence of actual magnets which introduces the idea of pole at all, other than as in Ampère's purely mathematical directrix of electrodynamic action; and the above considerations seem to show that this result is only obtained at the cost of preferring the fulfilment of the practically composite relation (A) to that of the fundamental electromagnetic relation (2), in the specification of an electrostatic system. This, though allowable if consistently adhered to, does not seem to be natural—if indeed the specification of a magnetic pole on an electrostatic system is a matter of importance at all.

The method indicated gives Maxwell's dimensions,  $L^{\frac{1}{2}} M^{\frac{1}{2}}$ .

In practice, one would most probably investigate the dynamic relations of statical charges with a galvanometer, and not with an electro-dynamometer.

Queen's College, Galway,  
May 10, 1862.

LVII. *On the Dimensions of a Magnetic Pole in the Electrostatic System of Units. (Second Article.)* By Prof. J. D. EVERETT\*.

MY appeal for an explicit statement of Maxwell's definition of the unit pole in the electrostatic system has brought me several communications from correspondents; and the diversity between them is a sufficient proof of the necessity for such an appeal. My correspondents do not refer me to any explicit definition by Maxwell himself, but give investigations which they regard as substantially his and which lead to his result. Two of these investigations seem quite satisfactory, and show that Maxwell's result can be obtained with as much simplicity as that of Clausius. They are given under the heads I., II., below.

Before entering on the points in dispute with respect to the electrostatic system, I may premise that the definitions of the unit quantity of electricity, the unit current, the unit electromotive force (or difference of potential), and the unit resistance (all of which may be called purely electrostatic definitions), are not in question, but are accepted by all parties. The divergence begins when we attempt to express magnetic quantities in an electrostatic system; and different results may be obtained according to the particular relation between magnetism and electricity which we select as the guiding principle in our definitions. In a strict sense there is no such thing as an electrostatic unit of any magnetic quantity; since magnetism and its relations to electricity lie outside the domain of electrostatics.

There are three laws of nature any one of which may be used to connect electrical with magnetic units.

I. The *galvanometer law*, as I may for brevity call it, because it is the law which determines the force which a current passing through the coil of a galvanometer exerts upon either pole of the needle. This law, stated without any assumption as to units, is that the force varies directly as the length of the wire, the strength of the current, and the strength of the pole, and inversely as the square of the distance of the wire from the pole. We must therefore, in every system, have

Force =  $k_1 \times \text{Current} \times \text{Pole} \times \text{Length} \div (\text{Distance})^2$ , (1)  
 $k_1$  being a factor which depends on the system employed. Maxwell's unit pole may be defined by making  $k_1=1$ . This gives, for determining the dimensions of a pole,

$$\text{MLT}^{-2} = \text{Current} \times \text{Pole} \times \text{L}^{-1}.$$

\* Communicated by the Author.

But

$$\text{Current} = M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-2};$$

therefore

$$\text{Pole} = M^{\frac{1}{2}} L^{\frac{1}{2}},$$

which is Maxwell's result. This proof was supplied to me by Professor Larmor. Clausius alludes to such a proof as having been given by Maxwell, and objects to it on the ground that the force which a current exerts upon a pole is not an electrostatic but an electrodynamical force. But, inasmuch as this objection applies equally to all definitions of "the unit pole in the electrostatic system," not excepting that offered by Clausius himself, it cannot be admitted as valid when we are discussing the merits of one as against another.

Again, we may employ

II. The *magneto-electric law*, which determines the electromotive force produced by moving a conductor in a magnetic field. This law, when stated without any assumption as to units, is that the electromotive force is directly as the length of the conductor, the velocity of its motion resolved in a certain direction, and the intensity of the field. Hence, bearing in mind that the intensity of the field due to a single pole is directly as the strength of the pole and inversely as the square of the distance, we must have, in every system,

$$\begin{aligned} \left. \begin{array}{l} \text{Electromotive} \\ \text{force} \dots \end{array} \right\} &= k_2 \times \text{Length} \times \text{Velocity} \times \text{Pole} \div (\text{Distance})^2 \quad (2) \\ &= k_2 \times L \times LT^{-1} \times \text{Pole} \times L^{-2} \\ &= \text{Pole} \times k_2 T^{-1}. \end{aligned}$$

If we define our unit pole by the condition  $k_2=1$ , we have

$$\begin{aligned} \text{Pole} &= \text{Electromotive force} \times T \\ &= M^{\frac{1}{2}} L^{\frac{1}{2}} T^{-1} \times T \\ &= M^{\frac{1}{2}} L^{\frac{1}{2}}. \end{aligned}$$

This mode of obtaining Maxwell's result was in substance supplied to me by Professor Fitzgerald. So far we have no discrepancy.

On the other hand, we may employ with Clausius,

III. The *law of the magnetic shell*, which asserts the equivalence of a current to a magnet. Taking the simplest case—that of a current in a plane circuit—the law of nature is that the moment of the equivalent magnet is jointly proportional to the strength of the current and the area of the circuit. Hence, since the moment of the magnet is the product of the



strength of either pole by the distance between the poles, we must have, in every system,

$$\text{Pole} \times \text{Length} = k_3 \times \text{Current} \times \text{Area}; \quad . \quad . \quad (3)$$

that is,

$$\text{Pole} = k_3 \times \text{Current} \times L,$$

where  $k_3$  depends on the system employed. Clausius defines his unit pole by making  $k_3=1$ , and thus obtains

$$\begin{aligned} \text{Pole} &= \text{Current} \times L \\ &= M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-2} \times L \\ &= M^{\frac{1}{2}} L^{\frac{5}{2}} T^{-2}. \end{aligned}$$

This result disagrees with that of the two preceding investigations; and hence the two equivalent assumptions  $k_1=1$ ,  $k_2=1$  are inconsistent with the assumption  $k_3=1$ . Maxwell has chosen the former alternative, Clausius the latter. On Maxwell's system we have

$$k_1=1, \quad k_2=1, \quad k_3=T^2 L^{-2}.$$

On Clausius's system we have

$$k_1=T^2 L^{-2}, \quad k_2=T^2 L^{-2}, \quad k_3=1.$$

In fact it can be shown that, if  $v$  be the ratio of the electromagnetic to the electrostatic unit of quantity of electricity,  $k_3$  would be  $\frac{1}{v^2}$  on Maxwell's system, and  $k_1$  and  $k_2$  would each be  $\frac{1}{v^2}$  on Clausius's system. When we bear in mind how frequently laws I. and II. are applied in practical calculation, and how extremely rare is any practical application of law III., it seems clear that, if we were driven to employ an electrostatic system in calculations relating to magnetism, the best choice we could make would be Maxwell's.

It is further clear that electrostatic systems are essentially inconvenient for calculations relating to electromagnetism. The electromagnetic system makes  $k_1$ ,  $k_2$ , and  $k_3$  each unity, and also gives the value unity to the factor  $k_4$  which occurs in the general expressions for the attractions and repulsions between currents. For example, the force with which two parallel currents, one of very great length and the other of length  $l$ , attract or repel each other, is given in any system by the formula

$$\text{Force} = k_4 \times \text{Product of currents} \times 2l \div \text{Distance}, \quad . \quad (4)$$

where  $k_4$  has the value unity in the electromagnetic system, and the value  $\frac{1}{v^2}$  in the electrostatic system, there being here no difference between Maxwell and Clausius.

The mutual force of two magnetic poles is

$$k_5 \times \text{Product of poles} \div (\text{Distance})^2, \quad . \quad . \quad (5)$$

where  $k_5$  is  $v^2$  in the electrostatic system of Maxwell, and  $\frac{1}{v^2}$  in that of Clausius, but is defined as unity in the electromagnetic system.

On the other hand, the mutual force of two charges of electricity is

$$k_6 \times \text{Product of charges} \div (\text{Distance})^2, \quad . \quad . \quad (6)$$

where  $k_6$  is defined as unity in the electrostatic system, but has the value  $v^2$  in the electromagnetic system.

A comparison of the foregoing six equations shows how cautious we ought to be in asserting that a particular dimensional relation "must hold in every system of units." The laws of nature which connect dissimilar quantities are laws of *proportion*, and it is only by convention that they can be stated as laws of *equality*. Clausius was in error in the assertion, which I adopted from him in my last communication, that in every system the product of the current by the area enclosed must be *equal* to the moment of the equivalent magnet. *Proportional* would be the correct word; and the factor  $k_3$ , which remains constant as the current and area vary, does not necessarily retain the same value when we pass from one set of units of length and time to another. Maxwell says (§ 482):—"It has been shown by numerous experiments . . . . that the magnetic action of a small plane circuit . . . . is the same as that of a magnet . . . . whose magnetic moment is equal to the area of the circuit multiplied by the strength of the current;" but the passage occurs in a discussion in which the "Electromagnetic system of measurement" is employed and defined (see § 479). I do not think that the charge of mistake brought against Maxwell has been substantiated. The controversy, however, has done good in exposing the difficulties and dangers which lurk in applications of electrostatical units to magnetism.

LVIII. *Action of Free Molecules on Radiant Heat, and its Conversion thereby into Sound.* By JOHN TYNDALL, F.R.S.\*

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§ 1. *Introduction.*

THE experimental researches of Rumford and Leslie raised the subject of Radiant Heat to an extraordinary pitch of interest and importance. Both of these philosophers occupied themselves with what may be called superficial emission and absorption.

Melloni is to be regarded as the founder of our knowledge of the transmission of radiant heat through solids and liquids. Save in a passing inference, to be noticed immediately, Melloni left untouched the gaseous form of matter—thinking, probably, that gases and vapours, though their diathermancy could hardly be supposed theoretically perfect, came in this respect so near perfection as to be placed beyond the grasp of laboratory experiment. It was doubtless the general prevalence of this conviction which caused this field of inquiry to lie fallow for so many years after the discovery of the thermo-electric pile.

By an experimental arrangement characteristic of the genius of the man, though, it may be, not quite equal to the requirements of the problem, Melloni proved that the law of inverse squares held good for radiant heat *in air*; and from this he inferred the absence of all sensible absorption, by air, within the distance embraced by his experiments †. Melloni extended to radiation his conclusion regarding absorption. “On ne connaît,” he writes, “aucun fait qui démontre directement le pouvoir émissif des fluides élastiques purs et transparents” ‡. Such was Melloni’s relation to the subject now before us.

\* Communicated by the Author, having been read before the Royal Society, January 23, 1882. The substance of this paper was delivered orally as the Bakerian Lecture on November 24, 1881.

† “Pour un intervalle de cinq à six mètres, l’air n’exerce aucune absorption sensible pour le rayonnement des corps chauds.”—*La Thermochrose*, p. 136.

‡ *Annales de Chimie et de Physique*, vol. xxii. p. 494.

In 1855 Dr. Franz, of Berlin, published a paper "On the Diathermaney of certain Gases and Coloured Liquids"\*. He found that air contained in tubes 452 and 900 millimetres long, absorbed 3.54 of the radiation from an Argand lamp; and he concluded that all transparent gases would behave like air. I have given reasons for holding that Dr. Franz in these experiments did not touch the question in hand †. In the arrangement which he describes, the absorption by air was quite insensible. But 60 per cent. of the radiation from his powerful source was lodged in the glass ends of his tubes; these, as secondary sources, radiated directly and indirectly against his pile; and it was their chilling by the cold air that slightly lowered his deflection and produced the supposed absorption.

It is not improbable that other attempts were made to bring gaseous matter under the dominion of experiment; but none to my knowledge are recorded.

## § 2. *Partial Summary of previous Work.*

My researches on magne-crystalline action carried with them the incessant use of conceptions and reasonings touching molecular constitution and arrangement. At an early period of these studies it occurred to me that heat, both in its radiant and in its ordinary thermometric form, might be turned to good account as an explorer of molecular condition. The first fruit of this idea was a paper "On Molecular Influences" ‡, in which it was shown that wood possesses three axes of calorific conduction coincident with the axes of elasticity discovered by Savart. Experiments on certain crystals recorded in this paper suggested a possible connexion between diathermaney and conductivity; and in 1853 I worked at this question. The substances then submitted to experiment were rock-crystal, amethyst, topaz, beryl, rock-salt, smoky quartz, fluor spar, tourmaline, Iceland spar, dichroite, arragonite, heavy spar, flint, and glass of various kinds. These minerals were employed in the shape of cubes carefully cut and polished, the transmission through each of them, in different directions, both of radiant and conducted heat being determined.

A desire for completeness, not then attained, caused me to postpone, and finally to forego the publication of the results

\* Poggendorf's *Annalen*, vol. xciv. p. 337.

† Philosophical Transactions, 1861, vol. cli. p. 27, and elsewhere.

‡ Ibid. 1853, vol. cxliii. p. 217.

of this inquiry. It, however, kept alive reflections on the influence of molecular constitution on the phenomena of radiation and absorption. Encountered continually by the thought that in liquids and solids the pure molecular action was, or might be, hampered by cohesion, the desire to bring, if possible, free molecules under the dominion of experiment beset me more and more.

At the beginning of 1859 I definitely attacked this problem, meeting at the outset difficulties and negations the reverse of encouraging. But after some weeks of labour, I found myself in secure possession of the result, that gases and vapours exhibited, in relation to radiant heat, phenomena far more surprising than those observed by Melloni in liquids and solids. On the 26th of May, 1859, the subject was brought before the Royal Society\*; and on the 10th of June I was able, by illuminating the dial of a galvanometer and casting its image upon a screen, to demonstrate in the Royal Institution not only the fact of absorption, but the astonishing differences of absorption which gases and vapours equally transparent to light manifested in regard to radiant heat†.

The following gases and vapours were then examined:—Air, oxygen, hydrogen, nitrogen, carbonic oxide, carbonic acid, nitrous oxide, coal-gas, ammonia, olefiant gas, bisulphide of carbon, chloroform, benzol, iodide of ethyl, cyanide of ethyl, formate of ethyl, acetate of ethyl, propionate of ethyl, iodide of amyl, chloride of amyl, amylene, absolute alcohol, amylie alcohol, methylic alcohol, ethylic ether, ethylamylie ether, sulphuric ether, and some others. In the Philosophical Magazine for 1862 I have given samples of the results obtained with a few of these substances; and I will here confine myself to the remark that were the measurements there recorded multiplied a hundredfold, they would fall far short of the number actually executed in 1859.

With the view of compelling the feeblest gases and vapours to show, if they possessed it, their capacity to absorb radiant heat, the “method of compensation” was invented‡. Without prejudice to the delicacy of the galvanometer, this method enabled me to bring into play quantities of heat far greater than those ever previously invoked, my object being so to exalt the total radiation that a minute fraction of that total should reveal itself to experiment. By this method not only were the feebler gases and vapours coerced, but the vastness of the diathermic range, if I may use the phrase, was esta-

\* Proceedings of Royal Society, vol. x. p. 37.

† Proceedings of Royal Institution, vol. iii. p. 155.

‡ Philosophical Transactions, 1861, vol. cli. pp. 6 & 7.



blished with a clearness and an evidence unattainable by any other means then existent\*.

Notices of the investigation having appeared in many English and continental journals †, I was induced to defer the detailed publication of the experiments. The investigation itself had taught me the difficulties and dangers which beset it. These had reference both to the methods of experiment and to the purity of the substances employed. To secure the perfect constancy of the sources of heat, and the perfect steadiness of the galvanometer, when the flux of heat was powerful, involved a lengthened discipline. With neither gases nor vapours, moreover, was it easy to obtain uniform results. When generated in different ways, the action of the same gas would sometimes prove itself so discordant as to suggest to me the possible existence of novel allotropic conditions to account for such variations of behaviour. Two samples, moreover, of nominally the same liquid, would furnish vapours yielding results far too divergent to be tolerated. The drying apparatus also contributed its quota of disturbance. These anomalies were finally traced to the fact that an incredibly small amount of impurity, derived from the stronger gases or vapours, sufficed to disguise and falsify the action of the weaker ones. All this had to be learnt; and when learnt, I thought it desirable, for the sake of accuracy, not to publish the results which had been gained with so much labour, but to go once more, with improved appliances, over the same ground. This I did, though it involved the total abandonment of seven weeks' uninterrupted experimental work in 1859, of seven weeks' similar work in 1860, and of many fragmentary efforts. On the 10th of January, 1861, the memoir containing an account of the investigation was handed in to the Royal Society ‡.

\* With moderate total heats the method of compensation is extremely easy of application; but when the total radiation is very large, some discipline is required to keep the galvanometer-needle steady in its most sensitive position. With due training, however, perfect mastery over this difficulty may be obtained.

† Proceedings of the Royal Society, May 26, 1859; *Proceedings of the Royal Institution*, June 10, 1859; *Bibliothèque Universelle*, July 1859; *Cosmos*, vol. xv. p. 321; *Nuovo Cimento*, vol. x. p. 196; *Comptes Rendus*, 1859; and in other journals.

‡ Section 3 of the Bakerian Lecture for 1861 reveals some of the difficulties which beset the earlier stages of these inquiries. To secure strength of radiation and steadiness of the needle I passed from source to source, obtaining my temperatures in turn from water, oil, fusible metal, sheets of copper heated by regulated flames, and from other things. Approximate results were readily obtainable; but I aimed at a degree of accuracy which would render any material retraction afterwards unnecessary. Soundness of work I thought preferable to rapidity of publication.

The first point of importance established in 1859, and developed in the memoir just mentioned, was that already referred to, namely the fact of absorption and large differences of absorption. The second point—destined, I think, to throw light on the deeper problems of molecular physics, was the proof, that while elementary gases offered a scarcely sensible impediment to radiant heat, equally transparent compound gases exhibited, in many cases, an energy of absorption comparable to that of the most athermanous solids and liquids. Determining, for example, the action of a mechanical mixture of two elementary gases, it was proved that without altering either the quantity of matter, or its perfect transparency to light, the absorption of invisible heat might be increased many hundredfold by the passage of the constituents of the mixture into a state of chemical combination.

A similar deportment may be detected in liquids and solids. The quantity of iodine vapour generated at ordinary temperatures is so small that its action on radiant heat is, as might be expected, insensible. But iodine itself, when liquefied by a powerful solvent, behaves as an almost perfectly transparent body to the obscure calorific rays, even when it is able to extinguish totally the light of the sun. Liquid bromine is also highly diathermanous. The same may be said of phosphorus. In Melloni's table Sicilian sulphur comes next to rock-salt in transmissive power. A concentrated solution of sulphur in bisulphide of carbon exerts no sensible action on radiant heat. By fusing together iodine and sulphur Professor Dewar has produced a "ray-filter" which separates with extreme sharpness the visible from the invisible rays. The remarkable diathermancy of certain specimens of vulcanite, brought to light in the experiments of Mr. Graham Bell and Mr. Preece, is probably due to the sulphur they contain. Melloni showed that lampblack is to some extent diathermanous. But when a suitable source of heat is chosen, lampblack proves far more pervious to radiant heat than Melloni found it to be. An opaque layer of this substance transmits 41 per cent. of the radiation from a hydrogen-flame. Were the lampblack optically continuous, the transmission would, doubtless, be still greater. An opaque solution of iodine transmits 99 per cent. of the radiation from the same source; while a layer of pure water, 0·07 of an inch in thickness, transmits only 2 per cent. of the radiation from a hydrogen-flame. Such results indicate that a profound change in the relation of ponderable matter to the luminiferous ether accompanies the act of chemical combination.

One of my principal aims in the Bakerian Lecture of 1861

was to illustrate the hold which experiment had obtained of a subject previously considered intractable. The densities of the gases and vapours employed were therefore varied within wide limits. In the experimental tube first made use of, a full atmosphere of olefiant gas absorbed more than 80 per cent. of the entire radiation; and it was therefore evident that a small fraction of an atmosphere of such gas would exert a measurable action. On trial, it was found possible to measure the absorption of  $\frac{1}{10,000}$  of an atmosphere of olefiant gas. The action of this gas was determined at sixteen different densities, the absorption, as long as the density was very small, being accurately proportional to the quantity of gas present. Similar experiments were made, and similar results obtained with other gases. The action of sulphuric ether vapour upon radiant heat was proved to be still more powerful than that of olefiant gas. The vapour was first carried into the experimental tube by a current of dry air; and the pure vapour was afterwards examined at seventeen different densities. Bisulphide of carbon was tested at twenty different densities, amylene at ten, benzol at twenty, and so of the others.

Considering the views previously entertained regarding the diathermancy of gases and vapours, I was naturally impressed with these results. Sceptical when I first observed them, I scrutinized them closely, until repeated scrutiny abolished every doubt. For my own instruction I illustrated the action of the stronger gases and vapours in a variety of ways. Turning, for example, once rapidly round a cock connecting the exhausted experimental tube with a holder containing a powerful gas, the needle would fly aside, owing to the stoppage of the heat by the infinitesimal amount of gas which entered the tube during the rotation. Discharging a powerful gas or vapour in free air, between the source of heat and the thermopile, a similar energetic action would be produced by the perfectly invisible agent.

I was schooled in such actions before the thought of testing the omnipresent vapour of our atmosphere occurred to me. When it did occur, there was in my mind no *a priori* ground for supposing that its action would prove insensible: for why should I assume that  $\frac{1}{100}$  of an atmosphere of aqueous vapour would prove neutral, after I had proved a small fraction of this fraction, on the part of other gases and vapours, to be active? There was no reason for such an assumption on my part—nothing to deter me from hopefully submitting the question to experiment. I accordingly tested the water vapour of the atmosphere in which I worked, and found its

action on a first trial to be thirteen times that of the air in which it was diffused.

It is not uninteresting to compare this approach to the problem with that of a very distinguished man—the late Professor Magnus, of Berlin\*. Subsequent to me, he subjected the aqueous vapour of our atmosphere to an experimental test; but he made the experiment under the assured conviction that his result would be negative. “It could,” he says, “be foreseen with certainty that the small amount of aqueous vapour taken up by air at ordinary temperatures could exert no influence on the transmission.” I think it must be obvious that if Magnus had gone through the discipline to which I had been subjected, he would not have used this language. His mistake, however, was a natural one. In fact during the earlier stages of the inquiry my mind was exactly in the condition of his mind—I also thinking, until practically instructed to the contrary, that the action of aqueous vapour at ordinary temperatures must be immeasurably small. It is well known that Magnus tested his foregone conclusion, and found it verified; while I, on the other hand, as above stated, justified mine.

The various gases which had been examined in the experimental tube with regard to their powers of absorption, were next tested as regards their powers of radiation. Columns of the heated gases were allowed to ascend in free air, and to radiate against the pile. In this simple way the radiative power of “transparent elastic fluids” was for the first time established. The order in which the gases ranged themselves, in regard to radiation, was exactly the order of their absorptions. Here, as in other cases, I instructed myself by observing how gases might be made to play the part of solids. Permitting, for example, a film of one of the stronger gases to glide over a heated surface of polished silver, the radiation from that surface was augmented as it might have been by a coating of isinglass or lampblack.

A surmise has been mentioned regarding new allotropic conditions, as occurring to me amid the perplexities of my earlier experiments. In one instance, that of electrolytic oxygen, the surmise proved correct. My first experiments indicated that the modicum of ozone which went forward with the oxygen exerted four times the absorption of the gas in which it was diffused†. Subsequently, by changing the apparatus, and taking pains to augment the quantity of ozone,

\* In many respects my generous and helpful friend; but, in regard to this question, my steadfast antagonist for many years.

† Philosophical Transactions, vol. cli. p. 8.

the multiple rose successively from 4 to 20, 35, 47, 85, ascending finally to 136 \*. The behaviour of ozone was thus proved to be similar to that of molecules composed of heterogeneous atoms. Hence the conclusion, drawn at the time, that the molecule of ozone was formed of oxygen atoms so grouped as to render their action upon radiant heat virtually that of a compound body. This, it is needless to say, is the constitution now assigned to ozone.

With the view of including corrosive gases and vapours among the number of those examined, and for other reasons, the brass experimental tube was displaced by a tube of glass of the same diameter and nearly 3 feet long. The source of heat was also changed from a Leslie's cube containing boiling water, to a plate of copper against which a sheet of flame was permitted to play. Extraordinary precautions were found necessary to ensure perfect steadiness on the part of the flame. With this arrangement the practical inability of the elementary gases to absorb radiant heat was further illustrated and confirmed. Chlorine gas and bromine vapour, for example, were proved to be highly diathermanous.

At the pressure of an atmosphere it was found that the diathermic range of colourless gases extended from 1 to about 1000. The portion of gas first entering the experimental tube, having the whole heat to act upon, produced, as might be expected, the greatest effect, the increment of absorption (after a certain quantity of gas or vapour had entered) being infinitesimal †. It was therefore interesting to compare together the various gases at very small pressures. When the pressure was that of 1 inch of mercury the diathermic range was greatly increased, the absorption by olefiant gas being then at least 6000 times the absorption by atmospheric air.

With the changed apparatus the action of the aqueous

\* Philosophical Transactions, vol. clii, pp. 84, 85.

† This is well illustrated by an experiment on sulphuric ether vapour recorded in the Bakerian Lecture for 1861:—

Pressure.	Absorption.
1 inch.	214
2 inches.	282
3    "	315
4    "	330
5    "	330

The absorption of air being taken as unity, that of sulphuric ether vapour at 1 inch mercury pressure is here shown to be 214. When, however, vapour corresponding to a pressure of 4 inches was already in the experimental tube, the addition of another inch did not sensibly augment the absorption.



vapour of our atmosphere was again taken up, and proved to be, not 13 times, as I had at first supposed, but, on fairly humid days, at least 60 times that of the air in which it was diffused. When carefully dried air was caused to pass over moistened glass, and then carried into the experimental tube, the absorption was still greater.

A power has been claimed for mist or haze which has been denied to aqueous vapour; but in these experiments concentrated luminous beams, which would have infallibly brought into view the least trace of suspended matter, revealed no mist or dimness of any kind. It is, moreover, demonstrable that an amount of turbidity, rendered strikingly evident by a luminous beam, exerts only a fractional part of the action of the pure aqueous vapour. When well-dried air was led, not through water or over wet glass, but over bibulous paper, taken apparently dry from the drawers of the laboratory, the amount of vapour carried forward from the pores of the paper produced 72 times the absorption of the air which carried it. After five repetitions of the experiment, wherein the same air was carried over the same paper, a quantity of vapour was still sent forward capable of exerting 47 times the absorption of the air in which it was diffused.

Here the possible action of odours upon radiant heat naturally suggested itself. Many perfumes were accordingly subjected to examination, the odorous substance being in each case carried into the experimental tube by a current of dry air. Thus tested, pachouli exerted 30 times, cassio 109 times, while aniseed exerted 372 times the absorption exerted by the air in which it was diffused.

A novel method of exhibiting the absorption and radiation of gaseous bodies, the germ of which had been previously discovered\*, was illustrated and developed by the new apparatus. Suppose the experimental tube exhausted, and the needle, under the joint action of the two sources, to be at  $0^{\circ}$ . On admitting a strong vapour the usual deflection would occur. Suppose it to be 50 galvanometric degrees. Let dry air be now introduced until the experimental tube is filled. Although fresh matter is thus thrown athwart the rays of heat, the needle behaves as if the matter within the experimental tube had wholly disappeared. It sinks to zero, and not only so, but passes, say to  $50^{\circ}$ , on the other side.

After the first moments of perplexity succeeding the observation of this effect, its cause became clear. On entering the experimental tube the air, having its *vis viva* destroyed, was

\* Philosophical Transactions, vol. cli. p. 32.

heated dynamically. Incompetent to radiate itself, it imparted its warmth to the vapour, and this powerful radiator poured the heat thus received against the pile. This heat sufficed not only to neutralize the deflection of  $50^{\circ}$  due to absorption, and indicating cold, but to carry the needle up to  $50^{\circ}$  on the side of heat. So likewise, when the experimental tube was filled with mixed air and vapour, the needle being at  $0^{\circ}$ , a stroke of the pump, though opening a freer passage for the rays from the source, caused a deflection indicative not of heat, but of cold. Here, the vapour within the tube, being chilled by the dilatation of the air, the pile radiated its uncompensated warmth into the vapour and produced the observed deflection.

Such observations suggested a new means of demonstrating the absorption and radiation of heat by gases and vapours. Abandoning all external sources of heat, and permitting the various gases already examined to enter the experimental tube at a common velocity, they became self-heated and radiated against the pile. Their radiation, thus determined, corresponded exactly with the results obtained when heated columns of these gases were permitted to rise freely in the atmosphere.

Both the radiation and absorption of vapours were determined in the same manner. The external source of heat was abandoned, and a measured quantity of every vapour was introduced into the experimental tube. Through an orifice of fixed dimensions dry air was then permitted to enter the tube, where the destruction of its *vis viva* raised its temperature. The heated air warmed the vapour, which in its turn radiated the heat imparted to it against the pile. The deflection of the galvanometer declared the strength of this radiation. Absorption was determined by permitting the mixed air and vapour to dilate by a measured quantity, the pile being here the warm body, and the chilled vapour the absorbent. The order in which the vapours stood as regards absorption was here exactly the order of their radiation; while both absorption and radiation, thus determined, agreed with the results obtained by sending the rays from an external source of heat through the pure vapours in the experimental tube.

What has been called "vapour-hesion," whereby liquid films are produced, has been supposed to play a dominant part in my experiments. But it can hardly be imagined that an irregular action of this kind could produce results of such precision and consistency as those here recorded. Such results are, in my opinion, only compatible with the con-

clusion that the veritable radiators and absorbers are the molecules of the vapours. Apart from all experiment, the notion that vapours must act in this way comes commended to us by the proved, and conceded, deportment of gases. It would be unreasonable to admit that a compound gaseous molecule is active, and at the same time to affirm that a compound vaporous molecule is inert.

This hypothesis of liquid films formed on the interior surface of the experimental tube, and on the plates of rock-salt, becomes, I think, more embarrassed as we proceed. It depends on the unproved assumption that liquids possess powers of absorption which are denied to their vapours. To water and brine, for instance, Magnus largely concedes such powers, but not to aqueous vapour. That the state of aggregation exerts an influence is not denied; but that it is here the dominant factor is open to doubt. To admit this would be to concede that the seat of absorption is the molecule as a whole, to the practical exclusion of the constituent atoms of the molecule. For if the atoms exert any influence, the mere passage from the liquid to the vaporous condition, which separates the molecules from each other, but leaves them individually intact, cannot destroy their powers of absorption.

At an early stage of these researches the parallelism of liquid and vaporous absorption forced itself upon my attention. Thus my experiments on bisulphide-of-carbon vapour were connected with the deportment of liquid bisulphide, as set forth in Melloni's table. The vapours, moreover, of chloride of sulphur and chloride of phosphorus, whose liquids stand in Melloni's table next to bisulphide of carbon, were afterwards proved by me to possess a diathermancy corresponding to that of their liquids. After various references to this subject in preceding memoirs, a portion of the Bakerian Lecture for 1864 was devoted to its examination. Liquid layers enclosed between plates of transparent rock-salt were tested in regard to their diathermancy; and, for the sake of control and verification, they were employed in five different thicknesses. The vapours of these liquids were examined in quantities proportional to the quantity of liquid, the same quality of heat being applied both to liquids and vapours. By these experiments it seemed to me placed beyond a doubt that the liberation of the molecule from the liquid condition did not destroy its absorbent power, the order of absorption being proved to be precisely the same for liquids and their vapours. Ten different substances were shown at the time here referred to to follow this rule. The list has since been extended; and I am not acquainted with a single real exception to the rule.

Any reasoning, therefore, which ascribes a potent absorption to perfectly impalpable films, condensed on the surface of my apparatus, and which denies that absorption to the free molecules within the experimental tube, is in my opinion untenable.

The relation between liquids and their vapours here indicated is very thorough. It extends beyond the field of experiment which we have hitherto had in view. I have, for example, published some researches on the action of rays of high refrangibility on gaseous matter, and have shown, in a great variety of cases, that the molecules are shaken asunder by such rays. The actinic clouds, as I have called them, produced by this decomposition reveal vividly the track of the beam by which they are generated, and render it easy to observe the distance to which the action penetrates. In the case of nitrite of amyl, for example, the power of decomposition is soon exhausted, the actinic cloud ceasing abruptly at a point about 18 inches from the place where the beam enters the vapour. An experimental tube 3 feet long has therefore one half of its vapour shielded by the other half; and on reversing the tube, the shielded half comes instantly down as an actinic cloud. In the case of iodide-of-allyl vapour, on the other hand, the beam may pass through a charged experimental tube 5 feet long, fill it with an actinic cloud, and still effect decomposition in another tube placed beyond it. What is true of these vapours is true equally of their liquids; for while a layer of the liquid nitrite  $\frac{1}{8}$  of an inch thick prevents, when placed in the track of the beam, the decomposition of its vapour, a layer of the liquid iodide, of quadruple thickness, does not arrest the decomposition. The power, and the lack of power, to be penetrated to considerable depths is shared alike by the liquids and their vapours. Other, and still more subtle and penetrating illustrations of parallelism between liquid and vaporious absorption are mentioned in the Bakerian Lecture for 1864\*.

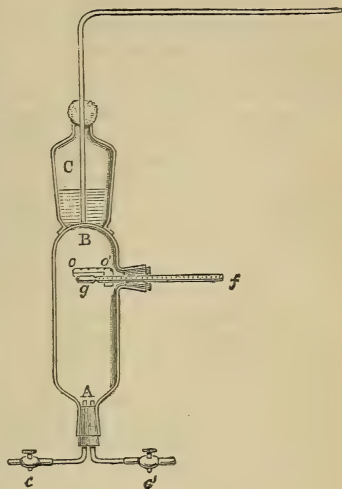
### § 3. *Researches of Magnus.*

Prompted by the experiment of Grove, illustrating the chilling action of hydrogen, Magnus, in 1860, began an in-

\* Carbonic acid is one of the feeblest of the compound gases, as regards the radiation from solid bodies; but for the radiation from a carbonic oxide flame it transcends all other gases in absorbent power. The action of aqueous vapour is also enhanced when it acts upon the rays emitted by a hydrogen-flame. The enhancement extends to water. Curious reversals of diathermic position, when heat from different sources is employed, are moreover shown to occur simultaneously with liquids and vapours.

vestigation on the power of gases to conduct heat\*. His apparatus, traced in outline from his own plate, is shown in fig. 1, where A B is the recipient for the gases, and C a flask containing water kept boiling by a current of steam. The bottom of C, which formed the top of A B, was the source of heat. A thermometer, *g f*, shielded by a cork or metal screen *o o'* from the radiation of the source, was intended to receive and measure the heat transmitted by conduction. The recipient A B was mounted in a space surrounded by water of a constant temperature. The heating of the thermometer when A B was exhausted†, was compared with its heating when A B was filled with various gases; and in every case but one the heating through the gas was found less than the heating through the vacuum. The exception was hydrogen, which carried more heat to the thermometer than was transmitted by the vacuum. The conclusion drawn by its author from this experiment was that hydrogen conducted heat like a metal.

Fig. 1.



One remark only in this Note has any reference to the diathermancy of gases; but it is a significant one. Magnus had no doubt as to the power of every one of his gases to conduct heat. There could, he supposed, be only a difference of degree between them and hydrogen. Whence, then, the

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\* A Preliminary Note of this inquiry is published in the *Bericht* of the Berlin Academy for July 30, 1860. No measurements are given; but certain results are announced. The experiments were first published in Poggendorff's *Annalen* for April 1861.

† This vacuum-temperature, at least in so far as it exceeded that of the sides of the recipient, was obviously derived from the screen.



lowering of the thermometer? He answers thus:—"From this it is not to be inferred that the gases do not conduct heat, but merely that in their case conduction is so feeble as to be neutralized by adiathermancy." These are the only words in the note which have any reference to radiation.

In his next inquiry Magnus dealt directly with the subject of diathermancy, a Preliminary Note of the investigation being published in the *Monatsbericht* for February 7th, 1861. This note, like its predecessor, consisted of general and descriptive statements, no actual measurements being given. The completed memoir was first published in Poggendorff's *Annalen* for April 1861. For the purposes of this new inquiry the apparatus used in the experiments on gaseous conduction was modified, as shown in fig. 2. To the recipient A B a second one G F was attached, the two being connected by the tubulure shown in the figure. The recipient G F rested upon the plate of an air-pump, on which also stood the thermopile *p*, with one of its faces turned towards the source. From the pile, through the air-pump plate, wires passed to the galvanometer. With this apparatus, the absorption by atmospheric air and by oxygen was found to be 11.12, and by hydrogen 14.1 per cent. of the total radiation. The alleged conductivity of hydrogen did not therefore manifest itself in these experiments.

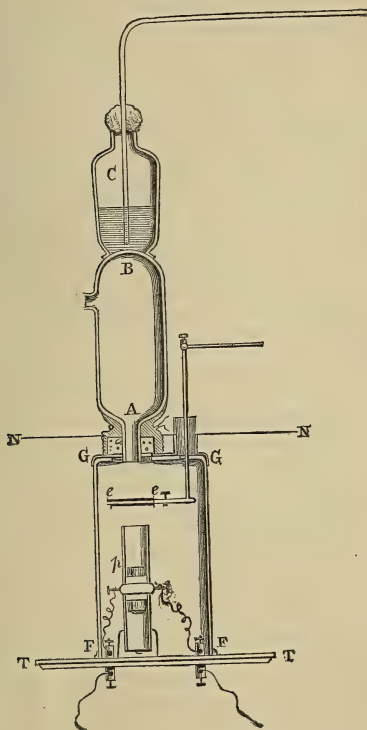
Let us analyze these results. In the first experiments the distance of the thermometer from the source of heat was 35 millimetres. The action on the thermometer through a vacuum being represented by 100, the action through air and through oxygen of this depth was found to be 82. The loss of 18 per cent. in air and in oxygen was alleged to be due to the adiathermancy of these media; to which percentage, if we wish to ascertain the *total* absorption by air, we should have to add such heat as reached the thermometer by conduction.

Turning now to the modified apparatus, which is evidently drawn to scale, the gas here traversed by the radiant heat was about 275 millimetres in depth, while the stratum traversed in the first experiments was, as stated, only 35 millimetres. Yet in these first experiments an absorption of 18 per cent., while in the later ones an absorption of only 11.21 per cent., is assigned to air. In other words, when the depth of the aerial stratum was augmented more than sevenfold, the absorption, instead of increasing, fell to less than two thirds of that of the shallower stratum. It is pretty obvious that an influence different from pure absorption came here into play. That influence was convection.

Anxious to probe this matter to the bottom, and to abolish,

or account for, the differences between my friend and myself, I wrote to him proposing an exchange of apparatus—that he should send his to London, and I mine to Berlin. I afterwards had a facsimile of his apparatus constructed in London,

Fig. 2.



and satisfied myself by actual trial that it was really hampered with the defects I had ascribed to it. By means of the striæ of incense smoke and of chloride of ammonium, the fact of convection in air was rendered plainly visible to the eye; while the behaviour of hydrogen, under like circumstances,

revealed the cause of its transporting more heat than the vacuum in the first experiments, and less heat, not only than the vacuum, but than air or oxygen, in the second experiments. In the one case the thermometer, being close to the source, came within the range of the convection-currents of this mobile gas, the heat being transported to it by these currents. In the other case a considerable distance intervened between the source and the pile, which was further effectually protected by the narrow tubulure. Through it the currents could not pass; but they nevertheless existed in the recipient A B, lowering the temperature of the source without heating the thermoscopic instrument.

The experimental resources of Magnus were great, and he here applied them; but the defects of his method were radical and irremovable. These defects reached their culmination in the subsequent researches of Professor Buff\*, who, by pursuing substantially the same method, arrived at the result that a stratum of air  $2\frac{1}{2}$  inches thick absorbed 60 per cent. of the radiation from a source of  $100^{\circ}\text{C}$ .† Buff also found olefiant gas to be more diathermanous than air; whereas at atmospheric pressures it is many hundred, and at a pressure of  $\frac{1}{30}$  of an atmosphere many thousand times more opaque to heat.

This is the point at which aqueous vapour enters into the experiments of Magnus. When dry and humid air were compared together in his apparatus, no difference between them was observed. But, apart from all disturbance, it would require an instrumental arrangement far more delicate and powerful than that here employed, to bring into view the action of a stratum of mixed air and aqueous vapour 11 inches deep, and having a temperature of only  $15^{\circ}\text{C}$ . Disturbances, however, were not absent. In the first place, the convection currents which enabled dry air to reduce the radiation by 11.12 per cent., were more than sufficient to mask the action of the vapour. Secondly, dry and humid air were brought in succession into direct contact with the face of the thermopile. The pile was therefore affected by any difference of temperature between it and the air, and it could scarcely be supposed that these temperatures were always alike. It was also affected by the condensation and evaporation which occurred when humid air and dry air were brought successively into contact with its lampblack-coated face. To "vapour-hesion" Magnus subsequently ascribed very large effects. Here we have the conditions specially suited to the development of the

\* Phil. Mag. 5th ser. vol. iv. p. 401. For my reply see Proc. Roy. Soc. vol. xxx. p. 10.

† Ibid. 1877, vol. iv. p. 424.

action, and yet no reference is made to it. Either, then, the disturbance was overlooked, or the apparatus was not sufficiently delicate to reveal it. To these two sources of disturbance (the lowering of the temperature of the source by convection, and the warming and chilling of the pile by contact, condensation, and evaporation) is to be added another, due to the warming which must have occurred when the dynamically heated air came into direct contact with the thermopile—an action which, in my apparatus, proved sufficient to whirl the needle of the galvanometer more than once through an entire circle.

Magnus next experimented with glass tubes 1 metre long and closed at the ends with plates of glass. His source of heat was a strong gas-flame aided, as in the experiments of Dr. Franz, by a parabolic mirror. Two tubes were employed, the one blackened within, and the other unblackened. With the blackened tube an absorption of 2.44 per cent. was found for air, and an absorption of 3.75 per cent. for hydrogen. In the unblackened tube the absorption by air was 14.75 per cent., and by hydrogen 16.27 per cent. of the total radiation.

I went over this ground with the utmost care, using invisible as well as visible heat. But, substituting plates of pellucid rock-salt for the plates of glass, I failed to realize the effect obtained by Magnus. He ascribed the difference between the results obtained with his blackened and his unblackened tube to a change of quality in the heat, produced by reflection from the interior surface of the latter. With plates of rock-salt, however, though the reflection abides, the change of quality does not occur. My position, therefore, in regard to these experiments is similar to what it was in regard to those of Dr. Franz. The results obtained with air, oxygen, and hydrogen were, I hold, due to the chilling of the heated glass ends of the tube by the cold gases, and the consequent lowering of the secondary radiation.

It was shown by Magnus himself, and is moreover obvious at first sight, that the unblackened tube sent a far greater amount of heat to the glass plate adjacent to the thermopile than the blackened one. That plate being more heated by the source, was more chilled by the air when it entered. The greater cooling-power of hydrogen accounts, moreover, for the advance of the supposed absorption from 14.75 to 16.27 per cent. With carbonic acid Magnus detected a difference which had escaped Dr. Franz. Instead of making the action of this gas equal to that of air, he found in the blackened tube an absorption of 8.19 per cent., and in the unblackened tube an absorption of 21.92 per cent., exerted by carbonic acid.

Here true absorption mixed itself with the effect of mere chilling, while with still more powerful gases the effect of chilling retreated by comparison more and more.

Such were the experiments which determined, in the first instance, the attitude of this distinguished man towards that portion of my work which related to the action of the air and vapour of our atmosphere on radiant heat. In the defence of his position he brought to bear all the resources of consummate skill and large experience. His position, however, was by no means a wholly defensive one. He dwelt repeatedly and emphatically on the dangers—and they are real—to which the method pursued by me was exposed. I had closed my experimental tube with plates of transparent rock-salt; and he urged against me the hygroscopic character of this substance. Placing rock-salt beside a vessel of water under a glass shade, he found that it could be rendered dripping wet\*. Hence his argument that, instead of measuring the action of vapour, I had really measured the action of brine. This, however, I could not admit. I was aware of the danger, and had avoided it. In many hundred instances the rock-salt plates had been detached from my experimental tube while filled with the very air which had produced the observed absorption, and found to be as dry as polished plate-glass. For a week at a time I have charged my experimental tube alternately with dried and undried air, removing every evening the plates of salt while the humid air filled the tube. Their dryness and polish were found unimpaired†. I have frequently flooded the experimental tube with light, and watched narrowly whether any dimness showed itself on the salt, or on the interior surface, when the humid air entered. There was nothing of the kind. I finally abandoned the plates of salt altogether, and obtained in a tube opened at both ends substantially the same effects as those obtained when the tube was closed with plates of rock-salt.

In 1862 Magnus came to London. He had been previously working at the points of difference between us, and had strengthened his first conviction. The action of the air he had found to be considerable, and the action of aqueous vapour practically nil. I also had been working, but with an entirely

\* It has been shown by Professor Dewar that the exposure of a dry plate of rock-salt for five minutes to saturated air sensibly augments the weight of the salt as determined by a delicate balance.

† This mastery over the apparatus was not attained without training. Any lapse of care soon declared itself by the condition of the plates of salt.



different result. It was hoped by both of us that our differences would be settled during this visit. With my closed experimental tube I showed him the neutrality of dry air and the activity of humid air; and while the latter was in the tube I detached the rock-salt plates and placed them in his hand. He closely inspected them, passed his dry handkerchief over them, and frankly and emphatically pronounced them perfectly dry. I then executed in his presence the experiments with the open tube, and reproduced the results which I had previously published. I subjected the method of compensation to a severe test, and showed him how exact it could be made. He frankly confessed his inability to find any flaw in my experiments, and, save in one particular, made no attempt to reconcile our differences. He accounted for the neutrality of dry air observed by me by pointing to my thermopile, between which and the experimental tube a space of air intervened. He argued, and justly argued, that though the calorific rays were permitted to enter the tube from a vacuum, if the air intervening between tube and pile could produce the effect which he ascribed to it, the heat would be robbed of its absorbable rays before the dry air entered the tube, the subsequent neutrality of dry air being a matter of course. The logic was good; but its basis I knew to be more than doubtful; and I therefore asked him whether a layer  $\frac{1}{20}$  of an inch thick between pile and tube would produce any sensible effect. His reply was an emphatic negative. In subsequent experiments, therefore, the conical reflector was removed from my pile, and placed within the experimental tube, its narrow end being caused to abut against the plate of rock-salt. The face of the pile was then brought within less than  $\frac{1}{20}$  of an inch of the rock-salt plate; and in this way my former measurements, which had declared the pure air of our atmosphere to be a practical vacuum to radiant heat, were verified to the letter.

The well-earned fame of Magnus as an experimenter, and his personal friendliness to myself, rendered it specially incumbent on me to deal respectfully with every one of his suggestions. He once intimated to me that the absorption, which I had supposed due to aqueous vapour, might be really due to the smoke and dust suspended in London air. To meet this I carried air myself from the Isle of Wight, had it carried from Epsom Downs and other places, and found the aqueous vapour diffused in such air to be from 60 to 70 times more energetic than the air itself. London air, moreover, was freed from its suspended matter, and tested when dry: it proved neutral. The self-same air was then rendered humid:

its absorbent power was restored. Then, with dry air as a carrier, I introduced smoke into the experimental tube, until it far exceeded in density that suspended in the London air when Magnus drew my attention to it. The quantity of heat intercepted by this smoke proved to be only a fraction of that absorbed by the perfectly invisible aqueous vapour.

On his return to Berlin he resumed his labours. He had been especially impressed by the experiments with the open tube; and to this point he directed his chief attention. "The result of this experiment," he writes, "was so surprising, and so little in accord with what I had found by other methods, that on reaching home I determined to repeat the experiment." He did so, with this result:—"I have," he says, "repeated the blowing-in of dry air and moist air many hundred times; but in no single case was the deflection such as to indicate a greater absorption by moist air"\*. Humid air, in his experiments, produced the deflection of heat; dry air the deflection of cold—a result diametrically opposed to mine. In London he had seen that my deflections were as large as I had affirmed them to be; but he had not criticised them with the view of ascertaining whether they were, or were not, in the right direction. In these new experiments, however, he had, he thought, hit upon their origin. The moving air had reached the face of the thermopile, producing, when humid, heat by condensation, and, when dry, cold by evaporation.

I read the account of these experiments with some concern; for it was thereby made plain to me that Magnus had by no means realized the anxious care that I had bestowed upon my work. The testimony of an independent observer would, I thought, set the matter right. My apparatus, carefully adjusted, was accordingly handed over to Dr. Frankland, who minutely tested every point involved in, or arising out of, the objection of Magnus. He verified all my results. His opinion as to the accuracy of the method of compensation is worth recording. "In conclusion," he writes, "I cannot but express my surprise and admiration at the precision and sharpness of the indications of your apparatus. Without having actually worked with it, I should not have thought it possible to obtain these qualities in so high a degree in determinations of such extreme delicacy"†. To this may be

\* Poggendorff's *Annalen*, 1863, vol. cxviii. p. 580; *Phil. Mag.* 1863, vol. xxvi. p. 25.

† The total heat here employed amounted to  $86^{\circ}2$  of a quadrant. This exceedingly large deflection was neutralized by the radiation from the compensating cube. But so accurately were the two sources balanced, and so constant was the radiation on both sides, that the determinations were made with ease, and without sensible disturbance or fluctuation.

added the subsequent testimony of Professor Wild, now of the University of St. Petersburg, who went carefully over the same ground. "In all my experiments," he says, "conducted according to Tyndall's method, which included more than a hundred distinct observations, I have never obtained deflections of the galvanometer-needle in contradiction to the statements of Professor Tyndall" \*.

In an extremely able paper, a translation of which is published in the *Philosophical Magazine* for October 1866, the Petersburg philosopher compares the methods pursued by Magnus and myself respectively. Insufficient sensitiveness, and the disturbance due to convection-currents, caused him, he says, to abandon the method of Magnus. "Although," he continues, "this method of investigating absorption may, in the hands of so experienced and expert an experimenter as Professor Magnus, be an appropriate one for determining absolute values with great certainty, I feel bound, from my own experience, to give a decided preference to Tyndall's method, not only on account of the greater facility with which it furnishes qualitative [quantitative] results, but also in consequence of its greater delicacy. It is principally in consequence of this greater delicacy that, notwithstanding the negative results furnished by Magnus's method, I maintain that the greater absorptive power of moist air, as compared with dry, has been fully established by the experiments made according to Tyndall's method; and I am of opinion that meteorologists may without hesitation accept this new fact in their endeavours to explain phenomena which hitherto have remained more or less enigmatical."

In 1866 Magnus varied his method of experiment, seeking to solve the question of absorption by observations on radiation. "I have," he says, "made a few determinations of the radiation of dry and moist air, and of some other gases and vapours. Up to the present time," he continues, "the capacity of these bodies to transmit heat has alone been determined" †. He then describes his arrangement:—"The gases and vapours were passed through a brass tube of 15 millimetres internal diameter, which was placed horizontally and heated by gas-flames. One end of the tube was bent upwards, so that the heated air ascended vertically, while at a distance of 400 millimetres from the vertical current was placed the thermopile." When dry air was sent through this tube, the deflection produced was three divisions of a scale; when air which had passed through water at a

\* *Phil. Mag.* 4th ser. vol. xxxii. p. 252.

† This is an inadvertence. Exhaustive experiments on the radiation of gases and vapours had been made and published many years previously

temperature of  $15^{\circ}$  C. was sent through the tube, the deflection rose to five divisions; when the water was warmed to  $60^{\circ}$  or  $80^{\circ}$  Fahr., the deflection was 20 divisions; and when the water boiled, the deflection was 100 divisions. In this last experiment, however, a mist appeared; so that, as urged at the time, the radiation could not be said to have been purely from vapour. In the other cases no mist was visible; but it was nevertheless concluded that the 20-division deflection was due to the formation of mist at the boundary of the ascending current.

I should be disposed to claim these experiments as telling in my favour. The first of them, in my opinion, dealt with the radiation, not from dry air, but from the adjacent aqueous vapour which had been warmed by the dry air. That the deflection in the second experiment was small is not surprising. The radiation which could reach the pile from a jet of air only 15 millimetres in diameter, and containing such moisture as could be taken up at  $15^{\circ}$  C., must have been extremely small under any circumstances. But in the present case, even this small radiation was diminished by the passage of the heat through 400 millimetres of undried air. I should demur to the explanation of the third experiment, and question the warrant to imagine a mist which could not be seen. Even the fourth experiment, where mist was visible, yielded, I doubt not, a mixed result—part of the effect, and probably the smallest part, being due to the mist, and part of it to the vapour.

With regard to the radiation from hot aqueous vapour, the following experiment is typical of some hundreds which I have had occasion to make. A burner, consisting of two rings provided with numerous small apertures, was placed within a square tin chimney. At some height above the burner the chimney was perforated, so as to enable the radiation from a heated gaseous column within the chimney to reach a distant thermopile. The side of the chimney facing the pile was so protected by screens that the radiation from the chimney itself was nil. Connecting the burner with a bottle of compressed hydrogen, the gas was ignited. A column of hot vapour rose from the burner and passed the aperture in the chimney through which it sent its rays to the pile. Mere tips of flame were first employed, the column of vapour rising from them sufficing nevertheless to produce a permanent deflection of

$40^{\circ}$ .

A slight augmentation of the flame sent the needle up to

$60^{\circ}$ .

A still further augmentation sent it up to

75°.

This last deflection was equivalent to more than 400 of the degrees in the neighbourhood of zero.

The radiating column was here considerably above the flame. To examine the condition of the column, a concentrated luminous beam was directed upon it. There was no precipitation. On the contrary, the suspended matter in the air of the chimney was much less than that of the surrounding air. Instead of a white mist, we had the blackness due to the destruction of the floating matter by the hydrogen-flame.

On quenching the flame, the needle returned accurately to zero.

In his objections Magnus, for the most part, dealt with true causes; but he erred as to their scope of action. I never denied the existence of the dangers which he emphasized. The hygroscopic character of rock-salt, for example, to which he recurred so often, cannot be questioned. It has a strong attraction for moisture, especially when cold. On this point my experience has been large; and I applied it in the execution of my experiments. These, as I have so frequently stated, were conducted with plates of salt as dry as polished glass or rock-crystal. Thus, while conceding the fact that rock-salt is hygroscopic, I demur to its application.

A similar remark applies to the last solution offered by Magnus of the differences between us. In 1867 he showed that vapours were condensed by surface-attraction to a greater extent than had previously been supposed. Blowing vapour-laden air into a metal tube, he found that heat was generated. He inferred, and rightly inferred, that this heat was produced by the condensation which occurred on the interior surface. This condensation he found to depend on the condition of the surface, being greater when it was tarnished or coated than when it was polished. He saturated air with moisture at a temperature of 16° C., and then raised both it and his pile to a temperature of 38°. When such air was blown against the dry face of the pile, heat was generated. Condensation therefore occurred upon a surface 22° C. higher than the dew-point of the vapour. Against this I have nothing to urge. But the fact by no means justifies the inference drawn from it, which was, that the vapours in my experimental tube were converted by "vapour-hesion" into liquid layers of high opacity to radiant heat; these layers, acting upon the calorific rays impinging on the interior surface of my tube, produced the absorption which I had erroneously ascribed to the



vapours. More than this, the liquid layers were supposed to be broken up into discontinuous patches, which not only absorbed the heat but scattered it. "Vapour-hesion," it may be added, was found to vary with the liquid which produced the vapour, being particularly strong in the case of alcohol.

Magnus brought this generalization to the test of experiment, but failed to verify it. He urged humid air against a dry mirror, from which radiant heat was reflected; but unless he wetted the mirror visibly, no effect was produced on the reflected beam. Still he held that reflection, oft repeated, rendered sensible an action which eluded a single reflection. My position here is clear. I do not doubt surface attraction, or deny the existence of impalpable films. No experiment was ever made on the reflection of light or radiant heat in which such films did not intervene; but they had as little effect upon my results as they had upon those of De la Provostaye and Desains\*, and of other refined experimenters. As early as 1859 I was made aware of the danger which might arise from condensation. Warned by the action of chlorine on my brass experimental tube, I coated it inside with lampblack, and retested with it all my vapours. The result removed from my mind the suspicion that surface condensation had any thing to do with the observed absorption. Many similar experiments with blackened tubes were subsequently made by me, for my own safety and instruction. There was no substantial difference between the results obtained with such tubes and those obtained with polished tubes in which internal reflection came into play.

Such are the general features and phases of a discussion which, though dealing only with a small item of my work, has consumed a considerable amount of time. Other able experimenters have entered this field, the latest of whom, MM. Lecher and Pernter, have published a long and learned memoir in Wiedemann's *Annalen*, which has been translated in the *Philosophical Magazine* for January 1881. My experiments with gases they corroborate, but not those with vapours. Regarding the action of aqueous vapour they are especially emphatic, their conclusion being "that moist air does not perceptibly absorb the heat-rays from a source of 100° C." In fact, they found moist air a little more transpa-

\* Considering the energy of water as a radiator, exceeding, according to Leslie, that of lampblack itself, the film of this liquid which must have covered the plates of silver in the experiments of the two French philosophers ought, if Magnus be correct, to have sensibly raised the emission. Calling the emission from lampblack 100, that from polished silver plus the film was only 2·1.

rent than a vacuum. "No imaginable source of error," they affirm, "has here been left out of account." The arrangement for filling with moist air was varied, the air allowed to stand for a long time over the water in the gas-holder, and this moist air then passed through several wash-bottles into the experimental space, but with the same *negative* result. In common with Magnus, MM. Lecher and Pernter ascribe my results to the condensation of liquid films on the rock-salt plates, and on the polished inner surface of my tube\*.

§ 4. *Experiments resumed: Verifications.*

With a view to my own instruction and to the removal of uncertainty from other minds, these researches on radiant heat were resumed in November 1880. A brass experimental tube 4 feet long,  $2\frac{3}{8}$  inches in diameter, and polished within, was first employed†. Interposed between it and the source was a "front chamber," through which, when exhausted, the rays passed into the experimental tube. A plate of transparent rock-salt separated the tube from the chamber, while a second plate of salt closed the distant end of the experimental tube. The source of heat was at first a Leslie's cube containing water at  $100^{\circ}$  C., to one of the faces of which the end of the front chamber was carefully soldered. The chamber also passed air-tight through a copper cell in which a continuous circulation of cold water was kept up. The heat which might otherwise have reached the experimental tube by conduction from the source was thus cut off. One face of a thermopile, provided with a reflecting cone, received the rays which passed through the experimental tube. The other face, also provided with a cone, received the rays from a "compensating cube," used, as formerly, to neutralize the radiation from the source, and to bring the needle of the galvanometer to zero when the experimental tube was exhausted. On the entrance, then, of

\* However I may otherwise differ from MM. Lecher and Pernter, I agree with their opening remark, that few other questions of experimental physics present difficulties so great as the one here under consideration. Nor do I see reason to differ from their closing words, that "the extraordinary difficulty of investigations of this sort would be richly repaid by the attainment of quantitative results; whilst the corresponding optical investigations (immeasurably easier) will always remain more of a qualitative nature." It is the difficulty here signalized that has caused so many distinguished investigators to go astray in this field of inquiry. I may state here that on the receipt of their paper I wrote to MM. Lecher and Pernter, but my communication was returned from Vienna through the dead-letter office.

† The plate answering to this description will be found in the *Philosophical Transactions* for 1861.

any absorbent gas or vapour the equilibrium was destroyed, the needle moved from zero; and from the observed permanent deflection the absorption was calculated. Other qualities of heat, and other experimental tubes than that here described, were afterwards introduced into the inquiry.

I here give the measurements executed in 1880 with the vapours of nine different liquids, in experimental tubes of the dimensions above given.

TABLE I.

	Pressures.	Vapours.		Liquids. Red-hot spiral.
		Leslie's cube, vacuum.	Leslie's cube free.	
Bisulphide of carbon . . . .	.48 in. mer.	4.4	5.0	7.6
Chloroform . . . .	.36 "	12.8	12.9	28.8
Benzol . . . .	.32 "	14.8	15.0	44.5
Iodide of ethyl . . . .	.36 "	18.4	19.3	47.0
Iodide of methyl . . . .	.46 "	25.0	26.2	59.0
Amylene . . . .	.26 "	26.1	27.2	65.0
Sulphuric ether . . . .	.28 "	35.0	35.6	71.0
Acetic ether . . . .	.29 "	43.3	43.7	77.5
Formic ether . . . .	.36 "	43.3	44.0	78.0

The "pressures" in this table are chosen with a view to the comparison of liquids and vapours. They express quantities of vapour which are proportional to the quantities of matter in the respective liquids at a common thickness. The two next columns contain the absorptions per 100 of the heat from two Leslie's cubes, the one with a vacuum in front of it, the other placed in free air and well protected from air-currents. The close agreement of the two columns proves the "front chamber" to be a superfluity. It also illustrates the coincidence to be attained in these measurements when they are carefully made. In the last column I have placed the absorptions exerted by liquid layers of the respective substances at a common thickness of one millimetre. The source of heat here was an incandescent platinum spiral. The order of absorption of liquids and vapours is the same.

This order is, as might be expected, undisturbed when we apply heat of the same quality to liquids and vapours respectively. This is shown by the following table:—

TABLE II.

	Polished tube.		Blackened tube.
	Spiral dull.	Spiral bright.	Spiral dull.
Bisulphide of carbon . . . . .	3.0	2.4	3.0
Chloroform . . . . .	7.0	4.6	5.0
Benzol . . . . .	9.4	7.5	10.0
Iodide of ethyl . . . . .	13.6	8.6	12.3
Iodide of methyl . . . . .	15.6	10.7	13.8
Amylene . . . . .	20.6	14.3	17.5
Sulphuric ether . . . . .	27.0	21.0	23.8
Acetic ether . . . . .	33.0	23.0	29.0
Formic ether . . . . .	33.0	23.0	30.0

The vapour-pressures here are the same as those employed in Table I. The order of absorption is the same in both tables; but its amount is diminished. This was to be expected, from the difference in the quality of the heat. We are dealing with transparent vapours—in other words, vapours pervious to the luminous rays; and the greater the proportion of these rays in the calorific beam, the less will be the absorption. This is well illustrated by the second column in the table, which shows the fall of the absorption when the spiral is raised from a dull red to almost a white heat. The polished tube was used in both these cases.

The third column of figures in Table II. shows the results obtained when the experimental tube was coated within with lampblack. The absorptions are in the same order, and almost of the same amount as those of the first column. The case is representative, and might be multiplied to any extent. It is incompatible with the notion that my results were due to films collected on the polished interior surface of my experimental tube.

Placing the substances recently experimented on in the order of their absorption, and also in the order which they exhibited in 1864, we have the following two columns:—

1880.	1864.
Bisulphide of carbon.	Bisulphide of carbon.
Chloroform.	Chloroform.
Benzol.	Iodide of methyl.
Iodide of ethyl.	Iodide of ethyl.
Iodide of methyl.	Benzol.
Amylene.	Amylene.
Sulphuric ether.	Sulphuric ether.
Acetic ether.	Acetic ether.
Formic ether.	Formic ether.

In 1864, therefore, the iodide of methyl proved itself more diathermanous than the iodide of ethyl, while both of them were more diathermanous than benzol. In 1880 the case was precisely the reverse. Suspecting that the discrepancy might be due to impurity, I requested my friend Professor Dewar to subject the liquids to a further process of purification. Tested afterwards, they produced the following deflections:—

	A.	B.	C.
Bisulphide of carbon . . . . .	5°0	5°0	4°0
Chloroform . . . . .	17°0	15°0	6°0
Iodide of methyl . . . . .	39°4	33°0	8°0
Iodide of ethyl . . . . .	33°0	35°0	12°5
Amylene . . . . .	42°0	41°0	16°0
Sulphuric ether . . . . .	44°3	43°5	18°2
Acetic ether . . . . .	46°2	45°5	22°0
Formic ether . . . . .	47°5	46°9	22°2

Under A and B respectively are the deflections produced by the liquids prior to and after purification. The iodide of methyl falls from 39°·4 to 33°, while the iodide of ethyl rises from 33° to 35°. The relative positions occupied by the liquids in 1864 are thus restored. Benzol, however, remained permanently lower than before. Under C are the deflections produced by the vapours of the purified liquids. Here also the positions of the two iodides are reversed, vaporous absorption following the order of liquid absorption. I have frequently encountered cases of this character. The simultaneous change of diathermic position of liquid and vapour indicates that the foreign ingredient, whatever it was, possessed approximately the same volatility as the substance which it vitiated.

[To be continued.]

### LIX. *Notices respecting New Books.*

*Kant's Critique of Pure Reason: translated into English by F. MAX MÜLLER.* 2 vols. London: Macmillan and Co.

THIS translation of Kant's great work appears in commemoration of the Centenary of its first publication. In the second volume we have the work proper, namely, a translation of the first edition: and in the first volume we have a preface by the translator, an Historical Introduction by Prof. Noiré, and a translation of the supplements which were added by Kant to the second edition.

In his preface the eminent translator states why he thought he might translate Kant's Critique, why he thought he ought to do it,



why a study of the work in question seemed necessary at present, what he considers the relation of Kant's *Metaphysic* to *Physical Science*, and in what manner Kant's *Philosophy* has been judged by *History*. As regards the first point, it may well be asked where could a philosopher more happily fitted for the task be found; and as regards the second, it is most interesting to learn the extent to which the Professor's own life-work has been influenced by the *Critique*. As regards the fourth point, the translator says:—"Metaphysical truth is wider than physical truth; and the new discoveries of physical observers, if they are to be more than merely contingent truths, must find their appointed place and natural refuge within the immovable limits traced by the metaphysician. It was an unfortunate accident that gave to what ought to have been called *pro-physical*, the name of *metaphysical science*; for it is only after having mastered the principles of *metaphysic* that the student of nature can begin his work in the right spirit, knowing the horizon of human knowledge, and guided by principles as unchangeable as the pole star" (p. xxxii). Prof. Max Müller, notwithstanding his great authority, will get few natural philosophers to agree with what he here lays down. On more than one occasion that which the metaphysician has pronounced to be impossible has been that which the physicist has accomplished. For instance, as was pointed out by Sir John Lubbock in his Address as President of the British Association (p. 29), Comte laid it down as an axiom regarding the heavenly bodies, that "*Nous concevons la possibilité de déterminer leurs formes, leurs distances, leurs grandeurs et leurs mouvements, tandis que nous ne saurions jamais étudier par aucun moyen leur composition chimique ou leur structure minéralogique.*" That was in 1842; and now, in 1882, there exists an elaborate science of Solar and Stellar Physics due to the method of Spectrum Analysis. Just above the place quoted, Professor Max Müller asks, "But how can any one who weighs his words say that the modern physiology of the senses has in any way supplemented or improved Kant's theory of knowledge? As well might we say that Spectrum Analysis has improved our logic." It is evident that Spectrum Analysis would have been capable of improving Comte's logic. If it be objected that Comte was not a true but a false metaphysician, we quote in reply what Professor Max Müller states at p. xxi:—"Even Comte, ignorant as he was of German and German philosophy, expressed his satisfaction and pride when he discovered how near he had, though unconsciously, approached to Kant's philosophy." The majority of scientists will probably fail to see any misfortune in the name *metaphysical*, but, on the contrary, hold that a theory of knowledge, to be of any value, must be dictated by the exact and natural sciences; that such a theory may dictate back to the sciences, and they may re-dictate to it; and that it is only by a mutual development of this kind that either can be made to approach perfection.

Professor Noiré, in his Introduction, traces the course of

philosophy through ancient and modern times, ending with Hume. He concludes with the following estimate of Kant; and from this estimate one may infer the point of view from which the great thinkers of ancient and modern times have been surveyed:—"It is therefore not too much to say that Kant is the greatest philosophical genius that has ever dwelt upon earth, and the 'Critique of Pure Reason' the highest achievement of human wisdom."

In this notice we have not the requisite space for discussing the Critique itself; but we may state briefly certain fundamental objections which may, it appears to us, be urged against it. The following extract indicates in a summary manner Kant's fundamental position. "Even if we remove from experience everything that belongs to the senses, there remain nevertheless certain original concepts, and certain judgments derived from them, which must have had their origin entirely *à priori*, and independent of all experience, because it is owing to them that we are able, or imagine we are able, to predicate more of the objects of our senses than can be learnt from mere experience, and that our propositions contain real generality and strict necessity, such as mere empirical knowledge can never supply" (p. 2). His object is to make a complete inventory of this *à priori* knowledge. "Whatever the understanding possesses, as it has not to be looked for without, can hardly escape our notice, nor is there any reason to suppose that it will prove too extensive for a complete inventory" (p. 11). "It is true that our Critique must produce a complete list of all the fundamental concepts which constitute pure knowledge" (p. 12). The inventory of the elements of transcendental æsthetic consists of two—namely, space and time; motion is rejected on the ground that it presupposes something empirical—the perception of something moving. But if we turn to Modern Science, which for the present purpose means *Thomson and Tait's Treatise on Natural Philosophy*, we find that there is a branch of Pure Mathematics, called Kinematics, which treats of the circumstances of mere motion considered without reference to the bodies moved. Its fundamental ideas are Velocity and Acceleration, neither of which involves the conception of Mass. If Space and Time only are *à priori*, how is it that Space, Time, and Mass are treated of by writers on Dynamics as the three fundamental ideas?

Kant was a mathematician; otherwise the Critique would not have been written. The influence of his study of the Mathematics is apparent everywhere. He views that science as so much *à priori* knowledge. "How far we can advance independently of all experience in *à priori* knowledge is shown by the brilliant example of Mathematics" (p. 4). "In the same manner all geometrical principles, *e. g.* that in every triangle two sides together are greater than the third, are never to be derived from the general concepts of side and triangle, but from an intuition, and that *à priori*, with apodictic certainty" (p. 22). That geometrical principles cannot be evolved out of mere definitions would not require to be denied,

had it not actually been held by some philosophers. Mathematicians will also agree with Kant in the stress which he lays upon the construction. But there is one point which it seems to us has not been dwelt upon sufficiently. Let us take Euclid, i. 16. If we examine the proof, we shall find that it turns upon the assertion that the angle ACF is less than the angle ACD. Now this may be easily asserted for a particular triangle; but before we can assert it for any triangle, we have to investigate the matter and glance over all the possible cases. If this be intuition, then it is hard to distinguish intuition from the process of generalization which the mind goes through in forming general judgments which Kant would characterize as empirical, such as that contained in the last clause of the following sentence:—"We know nothing but our manner of perceiving them, that manner being peculiar to us, and not necessarily shared in by every being, *though, no doubt, by every human being*" (p. 37).

Since Kant's day the domain of Mathematics has been greatly extended, and subjects formerly treated in a manner which was truly empirical are now treated in a manner which is exact. That domain includes even his own science of Logic. If, then, that vast body of knowledge is to be put down as *à priori*, by *à priori* can be meant nothing else than *exact*. If the Modern Logic, as developed and expounded by De Morgan, Boole, Harley, Jevons, Macfarlane, and Venn in this country, by Halsted and Pierce in America, and by Schröder in Germany, be sound science, then Kant's 'Critique' must contain considerable imperfections; for it proceeds on the assumption that the scholastic logic was perfect. "I mean only to treat of reason and its pure thinking, a knowledge of which is not very far to seek, considering that it is to be found within myself. Common logic gives an instance how all the simple acts of reason can be enumerated completely and systematically" (p. xxiv). "That Logic, from the earliest times, has followed that secure method may be seen from the fact that since Aristotle it has not had to retrace a single step, unless we choose to consider as improvements the removal of some unnecessary subtleties, or the clearer definition of its matter, both of which refer to the elegance rather than to the solidity of the science. It is remarkable also, that to the present day it has not been able to make one step in advance, so that, to all appearance, it may be considered as completed and perfect" (Sup., p. 364). Whence are the Pure Concepts of the Understanding (the Categories) obtained? From a classification of judgments "differing in some, though not very essential, points from the usual technicalities of logicians." The classification according to Quantity is Universal, Particular, Singular. It may be asked, What of doubly universal judgments, such as, for example, *Κρῆτες ἀεὶ ψεύονται*? It may be pointed out that we may have judgments universal with respect to both Space and Time, or with respect to Space only, or with respect to Time only, or with respect to neither. But the proper

objection is, that the number of logical forms frequently occurring in judgments is by no means so small as stated by the old logicians. They have no proper place for the equations of Algebra, or for statements about Relationships. In what intelligible sense can  $7+5=12$  be called a singular judgment? (p. 145). The list of the categories, being derived from an imperfect list of logical forms, cannot be perfect. It may be described, to use one of Kant's own phrases, as the result of a search after pure concepts undertaken haphazard, the completeness of which, as based on induction only, can never be guaranteed.

*Lessons on Form.* By R. P. WRIGHT, *Teacher of Mathematics, University College School, London.* 8vo, pp. 103. Longmans and Co.: 1882.

THIS short treatise aims at teaching the first elements of Geometry in an informal manner, as compared with the martinetism of Euclid, after the method of Pestalozzi. Commencing with the forms of the principal regular solids, it passes to the analysis of the relations among straight lines intersecting one another, and of the angles which they thus make, whether two are parallels cut by a secant or whether no two are parallel. In the three chapters treating of these matters formal proofs are sparingly introduced, the treatment being rather descriptive than demonstrative. Chapter 4 is a short initiation into the study of the triangle: the conception of similar triangles, having commensurable sides, being early introduced. The subject of the varieties of the Quadrilateral and the method of measuring areas occupy the remaining two chapters of the First Part.

Part II. treats of the metrical properties of triangles, as depending on Pythagoras's Principle, of which several proofs are given. The consideration of regular Polygons and of the Circle, as their limit, closes the treatise.

From this brief analysis of the scheme and contents of the book, it will be seen that pupils who have been guided to master it intelligently will have acquired a considerable amount of Geometrical knowledge; and this, as it is hoped, with little or no drudgery. The skilful teacher will know how to select those parts particularly which seem most suited to the degrees of development and aptitudes of the learners. That he will find the book most helpful and suggestive in a mode of instruction out of the usual routine path will be evident. This smaller work may be regarded as introductory to Mr. Wright's larger and more formal 'Elements of Plane Geometry', now in its fourth edition, a fact which stamps it as a standard treatise.

LX. *Intelligence and Miscellaneous Articles.*

ON THE LIQUEFACTION OF OZONE.

BY P. HAUTEFEUILLE AND J. CHAPPUIS.

**M.** CAILLETET having placed at our disposal the apparatus he has set up at the Ecole Normale for the liquefaction of ethylene, as well as the whole arrangement which he employs in order to study the changes of state of what are called the permanent gases, we have been able to complete our first experiments upon the liquefaction of ozone.

The study of the conditions under which a sudden expansion determines the formation of a mist in a mixture of oxygen and ozone has permitted us to establish that pure ozone is less easily liquefied than carbonic acid; the addition of carbonic acid to that mixture furnishes by compression a liquid of a pale blue colour, which coloration we attributed to ozone liquefied at the same time as the carbonic acid. From all these facts we concluded that it was possible to obtain ozone in a liquid form, and that that liquid would be strongly coloured.

Those deductions have just been fully confirmed by experiment; for we have obtained ozone in liquid drops of a deep indigo-blue colour. This liquid has been preserved nearly thirty minutes under a pressure of 75 atmospheres; its vaporization is not very rapid, even under the atmospheric pressure.

The liquefaction was attained by compressing with about 125 atmospheres a mixture of oxygen and ozone contained in the test-tube of M. Cailletet's apparatus, which is terminated by a capillary tube recurved at its upper portion, permitting the descending branch to be immersed in a jet of liquid ethylene, lowering its temperature probably below  $-100^{\circ}$ . When the gas operated on contains not more than 10 per cent. by weight of ozone, the gas compressed with 125 atmospheres is not perceptibly coloured in the ascending branch, while the blue coloration is very distinct in all the refrigerated portion of the capillary tube.

Does this coloration depend on the presence of a mixed liquid formed of ozone and oxygen, or on that of a thin film of liquid ozone lining the interior of the capillary tube? The absence of a distinct meniscus leaves this question undecided; but, in favour of the first of these hypotheses, we have noticed that the coloration was not more intense in the lower than in the upper part of the refrigerated tube, and that a sudden expansion does not determine the formation of a mist, which so well indicates, in M. Cailletet's experiments, the passage from the gaseous to the liquid state.

The tube becomes instantaneously colourless in consequence of the expansion, and contains in the thin part which terminates it a liquid drop of a deep indigo-blue; the ozone contained in the mixture is almost all condensed in the sloping part; for a fresh compression with 125 atmospheres does not communicate to the tube any appreciable coloration.



Once the ozone is liquefied in the capillary tube, it remains in that state long enough, even under the pressure of the atmosphere, for it to be examined either through the liquid ethylene or the refrigerated tube being withdrawn for a moment from that liquid. The deep-blue liquid gradually diminishes in volume: the vaporization of the ozone is sufficiently slow, its diffusion sufficiently rapid, for the gas to appear colourless above the nearly black liquid; it is only at the moment when the last traces of the liquid disappear that one ascertains the production of an azure-blue gas. The vaporization of the liquid ozone would bring back the system to its initial state, if the ozone were not slowly decomposed by the mercury employed to compress the gases.—*Comptes Rendus de l'Académie des Sciences*, May 1, 1882, pp. 1249-1251.

ON THE ACTION OF TELEPHONIC CURRENTS UPON THE  
GALVANOMETER. BY M. DE CHARDONNET.

If, in the telegraphic circuit, the receiver be replaced by a very sensitive galvanometer, and the transmitter be influenced by means of a diapason, an organ-pipe, or the voice, no deflection is observed as long as the sound keeps the same intensity; but as soon as the sonorosity is increased or diminished, the needle is deflected: the direction of the deflection varies according to whether the amplitude of the vibrations of the sounding body is increasing or decreasing. The effect is more marked when the transmitter is shaken by a noise of short duration, such as a detonation, or by a body lightly tapped upon the vibrating plate. In this last case the galvanometer-needle leaps like the seconds-hand of a clock. The experiment also succeeds very well when the sounding body is briskly moved nearer to or away from the transmitter. These deflections appear, of course, much more distinctly when a microphone-transmitter, like Ader's, is employed; but they are visible with every kind of telephone.

The explanation appears very simple, at least for the whole of the facts collectively:—

As long as the oscillations of the vibrating plate retain the same amplitude, and consequently the same velocity, the currents induced alternately in the two directions at each complete vibration compensate each other's action upon the galvanometer, whether they emanate from an electromagnet or a microphone; but if the oscillations tend towards zero, for example, each odd semioscillation has more amplitude than the following even semioscillation, and the direct and the inverse induced currents no longer put in motion the same quantities of electricity. The residues, of the same sign at each complete oscillation, accumulate so as to deflect the needle: and the more rapidly the sound diminishes, the greater is the deflection. This is what experiment demonstrates.—*Comptes Rendus de l'Académie des Sciences*, March 27, 1882, t. xciv. p. 857.

THE  
LONDON, EDINBURGH, AND DUBLIN  
PHILOSOPHICAL MAGAZINE  
AND  
JOURNAL OF SCIENCE.

SUPPLEMENT TO VOL. XIII. FIFTH SERIES.

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LXI. *Preliminary Notice of the Results accomplished in the Manufacture and Theory of Gratings for Optical purposes.*  
By Prof. H. A. ROWLAND, of the Johns Hopkins University, Baltimore\*.

IT is not many years since physicists considered that a spectroscope constructed of a large number of prisms was the best and only instrument for viewing the spectrum where great power was required. These instruments were large and expensive, so that few physicists could possess them. Professor Young was the first to discover that some of the gratings of Mr. Rutherfurd showed more than any prism-spectroscope which had then been constructed. But all the gratings which had been made up to that time were quite small, say one inch square, whereas the power of a grating in resolving the lines of the spectrum increases with the size. Mr. Rutherfurd then attempted to make as large gratings as his machine would allow, and produced some which were nearly two inches square, though he was rarely successful above an inch and three quarters, having about thirty thousand lines. These gratings were on speculum-metal, and showed more of the spectrum than had ever before been seen, and have, in the hands of Young, Rutherfurd, Lockyer, and others, done much good work for science. Many mechanics in this country and in France and Germany have sought to equal Mr. Rutherfurd's gratings, but without success.

Under these circumstances I have taken up the subject with the resources at command in the physical laboratory of the Johns Hopkins University.

One of the problems to be solved in making a machine is to make a perfect screw; and this mechanics of all countries have sought to do for over a hundred years, and have failed. On thinking over the matter, I devised a plan whose details I

\* Communicated by the Author.

shall soon publish, by which I hoped to make a practically perfect screw; and so important did the problem seem, that I immediately set Mr. Schneider, the instrument-maker of the university, at work at one. The operation seemed so successful that I immediately designed the remainder of the machine, and have now had the pleasure since Christmas of trying it. The screw is practically perfect, not by accident, but because of the new process for making it; and I have not yet been able to detect an error so great as one one-hundred-thousandth part of an inch at any part. Neither has it any appreciable periodic error. By means of this machine I have been able to make gratings with 43,000 lines to the inch, and have made a ruled surface with 160,000 lines on it, having about 29,000 lines to the inch. The capacity of the machine is to rule a surface  $6\frac{1}{4} \times 4\frac{1}{4}$  inches with any required number of lines to the inch, the number only being limited by the wear of the diamond. The machine can be set to almost any number of lines to the inch; but I have not hitherto attempted more than 43,000 lines to the inch. It ruled so perfectly at this figure that I see no reason to doubt that at least two or three times that number might be ruled in one inch, though it would be useless for making gratings.

All gratings hitherto made have been ruled on flat surfaces. Such gratings require a pair of telescopes for viewing the spectrum. These telescopes interfere with many experiments, absorbing the extremities of the spectrum strongly; besides, two telescopes of sufficient size to use with six-inch gratings would be very expensive and clumsy affairs. In thinking over what would happen were the grating ruled on a surface not flat, I thought of a new method of attacking the problem; and soon found that if the lines were ruled on a spherical surface, the spectrum would be brought to a focus without any telescope. This discovery of concave gratings is important for many physical investigations, such as the photographing of the spectrum both in the ultra-violet and the ultra-red, the determination of the heating-effect of the different rays, and the determination of the relative wave-lengths of the lines of the spectrum. Furthermore it reduces the spectroscope to its simplest proportions, so that spectroscopes of the highest power may be made at a cost which can place them in the hands of all observers. With one of my new concave gratings I have been able to detect double lines in the spectrum which were never before seen.

The laws of the concave grating are very beautiful on account of their simplicity, especially in the case where it will be used most. Draw the radius of curvature of the mirror

to the centre of the mirror, and from its central point, with a radius equal to half the radius of curvature draw, a circle ; this circle thus passes through the centre of curvature of the mirror and touches the mirror at its centre. Now, if the source of light is anywhere in this circle, the image of this source and the different orders of the spectra are all brought to focus on this circle. The word focus is hardly applicable to the case, however; for if the source of light is a point, the light is not brought to a single point on the circle, but is drawn out into a straight line with its length parallel to the axis of the circle. As the object is to see lines in the spectrum only, this fact is of little consequence provided the slit which is the source of light is parallel to the axis of the circle. Indeed it adds to the beauty of the spectra, as the horizontal lines due to dust in the slit are never present, as the dust has a different focal length from the lines of the spectrum. This action of the concave grating, however, somewhat impairs the light, especially of the higher orders; but the introduction of a cylindrical lens greatly obviates this inconvenience.

The beautiful simplicity of the fact that the line of foci of the different orders of the spectra are on the circle described above, leads immediately to a mechanical contrivance by which we can move from one spectrum to the next and yet have the apparatus always in focus ; for we only have to attach the slit, the eye-piece, and the grating to three arms of equal length, which are pivoted together at their other ends, and the conditions are satisfied. However we move the three arms, the spectra are always in focus. The most interesting case of this contrivance is when the bars carrying the eye-piece and grating are attached end to end, thus forming a diameter of the circle, with the eye-piece at the centre of curvature of the mirror, and the rod carrying the slit alone movable. In this case the spectrum as viewed by the eye-piece is normal; and when a micrometer is used, the value of a division of its head in wave-lengths does not depend on the position of the slit, but is simply proportional to the order of the spectrum, so that it need be determined once only. Furthermore, if the eye-piece is replaced by a photographic camera, the photographic spectrum is a normal one. The mechanical means of keeping the focus is especially important when investigating the ultra-violet and ultra-red portions of the solar spectrum.

Another important property of the concave grating is that all the superimposed spectra are in exactly the same focus. When viewing such superimposed spectra, it is a most beautiful sight to see the lines appear coloured on a nearly white ground. By micrometric measurement of such superimposed spectra,

we have a most beautiful method of determining the relative wave-lengths of the different portions of the spectrum, which far exceeds in accuracy any other method yet devised. In working in the ultra-violet or ultra-red portions of the spectrum, we can also focus on the superimposed spectrum, and so get the focus for the portion experimented on.

The fact that the light has to pass through no glass in the concave grating makes it important in the examination of the extremities of the spectrum, where the glass might absorb very much.

There is one important research in which the concave grating in its present form does not seem to be of much use; and that is in the examination of the solar protuberances; an instrument can only be used for this purpose in which the dust in the slit and the lines of the spectrum are in focus at once. It might be possible to introduce a cylindrical lens in such a way as to obviate this difficulty. But for other work on the sun the concave grating will be found very useful. But its principal use will be to get the relative wave-lengths of the lines of the spectrum, and so to map the spectrum; to divide lines of the spectrum which are very near together, and so to see as much as possible of the spectrum; to photograph the spectrum so that it shall be normal; to investigate the portions of the spectrum beyond the range of vision; and, lastly, to put into the hands of any physicist at a moderate cost such a powerful instrument as could only hitherto be purchased by wealthy individuals or institutions.

To give further information of what can be done in the way of gratings I will state the following particulars:—

The dividing-engine can rule a space  $6\frac{1}{4}$  inches long and  $4\frac{1}{4}$  inches wide. The lines, which can be  $4\frac{1}{4}$  inches long, do not depart from a straight line so much as  $\frac{1}{100000}$  inch, and the carriage moves forward in an equally straight line. The screw is practically perfect, and has been tested to  $\frac{1}{100000}$  inch without showing error. Neither does it have any appreciable periodic error; and the periodic error due to the mounting and graduated head can be entirely eliminated by a suitable attachment. For showing the production of ghosts by a periodic error, such an error can be introduced to any reasonable amount. Every grating made by the machine is a good one, dividing the 1474 line with ease; but some are better than others. Rutherford's machine only made one in every four good, and only one in a long time which might be called first-class. One division of the head of the screw makes 14,438 lines to the inch. Any fraction of this number in which the numerator is not greater than, say, 20 or 30 can be



ruled. Some exact numbers to the millimetre, such as 400, 800, 1200, etc., can also be ruled. For the finest definition either 14,438 or 28,876 lines to the inch are recommended—the first for ordinary use, and the second for examining the extremities of the spectrum. Extremely brilliant gratings have been made with 43,314 lines to the inch; and there is little difficulty in ruling more if desired. The following show some results obtained:—

Flat grating, 1 inch square, 43,000 lines to the inch.

Divides the 1474 line in the first spectrum.

Flat grating,  $2 \times 3$  inches, 14,438 lines to the inch, total 43,314. Divides 1474 in the first spectrum, the E line (Ångström 5269.4) in the second, and is good in the fourth and in even the fifth spectrum.

Flat grating,  $2 \times 3$  inches, 1200 lines to 1 millimetre. Shows very many more lines in B and A groups than were ever before seen.

Flat grating,  $2 \times 3\frac{1}{4}$  inches, 14,438 lines to the inch. This has most wonderful brilliancy in one of the first spectra, so that I have seen the Z line, wave-length 8240 (see Abney's map of the ultra-red region), and determined its wave-length roughly, and have seen much further below the A line than the B line is above the A line. The same may be said of the violet end of the spectrum. But such gratings are only obtained by accident.

Concave grating,  $2 \times 3$  inches, 7 feet radius of curvature, 4818 lines to the inch. The coincidences of the spectra can be observed to the tenth or twelfth spectrum.

Concave grating,  $2 \times 3$  inches, 14,438 lines to the inch, radius of curvature 8 feet. Divides the 1474 line in the first spectrum, the E line in the second, and is good in the third or fourth.

Concave grating,  $3 \times 5\frac{1}{2}$  inches, 17 feet radius of curvature, 28,876 lines to the inch, and thus nearly 160,000 lines in all. This shows more in the first spectrum than was ever seen before. Divides 1474, and E very widely, and shows the stronger component of Ångström 5275 double. Second spectrum not tried.

Concave grating,  $4 \times 5\frac{3}{4}$  inches, 3610 lines to the inch, radius of curvature 5 feet 4 inches. This grating was made for Professor Langley's experiments on the ultra-red portion of the spectrum, and was thus made very bright in the first spectrum. The definition seems to be very fine, notwithstanding the short focus, and divides the 1474 line with ease. But it is difficult to rule so concave a grating, as the diamond marks differently on the different parts of the plate.

These give illustrations of the results accomplished; but of course many other experiments have been made. I have not yet been able to decide whether the definition of the concave grating fully comes up to that of a flat grating; but it evidently does so very nearly.

Baltimore, May 25, 1882.

LXII. *Crystallographic Notes.* By L. FLETCHER, M.A., of the Mineral Department, British Museum\*.

[Plate X.]

IX. *Skutterudite*.

THE first mention of this mineral was made in 1827 by Breithaupt†, to whom it had been submitted by his brother-in-law on returning from a voyage in Norway. Though none of the specimens presented crystal-faces, Breithaupt found that there were distinct cleavages parallel to the sides of a cube, for which reason he assigned to the species the name of Tesseral-Kies. Cleavages, more or less interrupted and indistinct, were found to exist parallel to planes truncating the edges and quoins of this cube, indicating that the crystallisation was that characteristic of the cubic system. Breithaupt went a step further, and, from traces of separation which manifested themselves in the direction of the octahedral planes, hazarded the conjecture, since (curious to say) verified, that the crystals would prove to present the octahedron as the predominant form. The specimens were of a bright metallic lustre and of a tin-white colour. The specific gravities of five different fragments were determined to be 6.659, 6.681, 6.718, 6.748, 6.848, and thus had a considerable range. As, however, after breaking up the fragments, it was seen that the first three included particles of quartz and actinolite, Breithaupt regarded the true specific gravity as lying between 6.748 and 6.848. The hardness was greater than that of cobaltite or Cobaltkies; and as blowpipe examination had indicated that cobalt and arsenic were the chief constituents, Breithaupt suggested the secondary title of Hartkobaltkies. The associated minerals were cobaltine, copper pyrites, glassy actinolite, serpentine, quartz, and sometimes also cobalt-bloom.

\* Communicated by the Author, having been read before the Crystallogical Society, May 30, 1881.

† "Ueber eine neue Kies-Species von Skutterud," Pogg. *Ann.* vol. ix. p. 115 (1827).

Ten years later Scheerer\* met with a mineral which examination led him to regard as identical with that previously described by Breithaupt. A quantitative analysis, afterwards confirmed by Wöhler†, gave the following result:—

Arsenic .....	77·84
Cobalt .....	20·01
Sulphur .....	0·69
Iron .....	1·51
Copper .....	traces
	<hr/> 100·05

a composition expressed by the formula  $\text{CoAs}_3$ .

The description given by Scheerer agrees very closely with that of Breithaupt; but not only did he find the mineral in its massive condition, but also as isolated crystals. These had the form of octahedra, modified by the cube dodecahedron and an icositetrahedron: the inclination of the faces of the latter form to the adjacent face of the octahedron, as measured, was  $19^\circ 27'$ , proving clearly that the icositetrahedron was (211), for which the calculated angle is  $19^\circ 28'$ ; the faces of this particular icositetrahedron truncate the edges of the dodecahedron. He further observes that this form (211) was present on every crystal he had examined. Scheerer notices also the interesting fact that the crystals are often found implanted upon crystals of cobaltite, and states that he had not been able to trace any regularity in the relative position of the crystals of the two species. As the term Tesseralkies might be taken to imply that the mineral crystallises in the form of cubes, he suggests Arsenikkobaltkies as a more appropriate name.

In Haidinger's 'Handbuch der bestimmenden Mineralogie' (1845) the mineral appears under still another title—Skutterudite, suggestive of the locality where the crystals are found.

In Brook and Miller's edition of 'An Elementary Introduction to Mineralogy by the late William Phillips,' published in 1852, the forms presented by Skutterudite are given as (100), (110), (111), and (221), and the angles according with this description are calculated. It will be observed that the form (211) described by Scheerer is not mentioned, but that a new form, (221), a triakisoctahedron, is substituted. In 1862 vom Rath‡, apparently not having referred to the

\* "Ueber zwei norwegische Kobalterze von den Skutteruder Gruben," Pogg. *Ann.* vol. xlii. p. 553 (1837).

† Pogg. *Ann.* vol. liii. p. 591.

‡ "Neue Flächen am Tesseralkies," Pogg. *Ann.* vol. cxv. p. 480.

original paper of Scheerer, and assuming that the information contained in the last-mentioned 'Mineralogy' incorporated all the results of observation up to that date, determined anew the form (2 1 1), and also added a triakisoctahedron (3 3 2), a tetrakisohexahedron (3 1 0), and a hexakisohctahedron (6 4 3).

The prominent forms, according to both Scheerer and vom Rath, are the octahedron (1 1 1), the dodecahedron (1 1 0), and the icositetrahedron (2 1 1); while, according to the latter mineralogist, the additional forms (3 3 2), (3 1 0), (6 4 3) are only subordinately developed. The disposition of the faces of this hexakisohctahedron (6 4 3) will be more easily imagined, if it be remarked that they cut off the edges of intersection of the octahedron with the tetrakisohexahedron (3 1 0). With regard to the faces of the triakisohctahedron, vom Rath observes that they are small and unsuited for measurement, but that in one case he had been able to measure the angle made with the adjacent face of the octahedron as lying between  $9\frac{1}{2}^{\circ}$  and  $10\frac{1}{2}^{\circ}$ ; whence he concludes that the form is not (2 2 1), as given by Miller, which requires an angle of  $15^{\circ} 48'$ , but (3 3 2), for which the calculated angle is  $10^{\circ} 2'$ .

As vom Rath considered it unlikely that the subordinate triakisohctahedron present on some crystals should be (2 2 1) and on others (3 3 2), he suggests that the symbol given by Miller is a mistaken one, and appears to think that the form (2 2 1) may have been determined by inspection and not by measurement. It seems, however, much more probable that the information given by Miller is intended to be merely a statement of the results of Scheerer, and not of a later examination by Miller himself, who could not have failed to remark the existence of the icositetrahedron (2 1 1), which is so characteristic that it was present on every crystal examined by Scheerer, and in fact can be distinguished on every specimen in the collection of the British Museum. It seems fairly evident, then, that Miller's (2 2 1) was a simple error introduced in the copying of Scheerer's results, and that the angles were afterwards calculated without this error in the translation of the symbol from the German notation being remarked. If this hypothesis be correct, (2 2 1) must be expelled from the list of observed forms.

The next mention of Skutterudite is to be found in an extremely interesting and important paper by Schrauf and Dana on the thermoelectric properties of mineral-varieties\*, where they remark that, although the mineral undoubtedly crystallises in the cubic system, and has never been observed to

\* "Ueber die thermoelektrische Eigenschaften von Mineral-Varietäten," *Sitz.-Ber. Ak. Wien*, vol. lxix. p. 153 (1874).

present any hemihedral development, they nevertheless find some specimens to be thermoelectrically positive and others negative.

The bearing of this remark will be more obvious when it is recalled to mind that the investigation of Schrauf and Dana was undertaken with a view to test the accuracy of the induction made by Gustav Rose from his experiments on iron pyrites and cobaltine\*—that the opposition in the thermoelectric behaviour of different specimens of the same mineral is due to the diplohedral hemisymmetry,—and of his inference that the faces observed on the positive and negative crystals belong only apparently to the same, really to complementary, semiforms. The observation of Schrauf and Dana, that the same thermoelectrical peculiarities are shown by a holohedral mineral of the same crystalline system to which iron pyrites and cobaltine belong, will clearly not strengthen the position taken up by Rose.

It is therefore of some interest to find that the specimens in this Collection prove that not only is Skutterudite undoubtedly hemihedral, but that it presents the particular variety of hemisymmetry which is so characteristic of both iron pyrites and cobaltine.

Brezina† has pointed out that the opposition of thermoelectric properties shown by various specimens of iron pyrites and cobaltine cannot be satisfactorily explained by diplohedral symmetry, and holds that haplohedral hemisymmetry must be at the same time present—that, in other words, the crystals must be tetartohedral in structure; and, assuming that the differences in the specimens are only differences of molecular grouping, Brezina regards iron pyrites and the allied species as being really tetartohedral—a view which as yet there is little, if any, crystallographic evidence to support. It seems, however, more probable that Schrauf and Dana are right in attributing this difference, not to crystalline hemisymmetry, but to slight differences of composition or of density; and the force of their argument will not be very much weakened by the reference of the symmetry of the crystalline forms of Skutterudite to a hemihedral type.

It may be useful to remark that attention was first directed to the hemihedry by the discovery of a crystal of Skutterudite among the specimens of that typically hemihedral mineral

\* "Ueber den Zusammenhang zwischen hemiëdrischer Krystallform und thermo-elektrischen Verhalten beim Eisenkies und Kobaltglanz," *Pogg. Ann.*, vol. cxlii, p. 1 (1871).

† "Ueber die Symmetrie der Pyritgruppe," *Tschermak's Min. Mittheil.*, p. 23 (1872).



cobaltine, to which it was very similar in habit, though different in colour. Closer examination, however, made known the fact that the hemihedrally-developed faces belonged, not to the pentagonal dodecahedron  $\pi(210)$ , so common in both cobaltine and iron pyrites, but to the much rarer form  $\pi(310)$ . In this Collection there are fourteen more or less perfect crystals, presenting respectively the following development:—

No. 1 shows only the octahedron  $o(111)$  modified by faces of the icositetrahedron  $n(211)$ , as shown in fig. 1 (Pl. X.).

Nos. 2, 3, 4 show also the faces of the dodecahedron  $d(110)$ , and are represented in fig. 2—each of these four crystals being implanted upon a crystal of cobaltite in the way described by Scheerer and vom Rath. On Nos. 5 and 6 the same forms recur; but some of the quoins are truncated by small planes of the cube  $a(100)$ , probably due to cleavage.

As in all the above forms the poles of the faces lie in dodecahedral planes, the abeyance of symmetry of the latter would have no effect in reducing the number of faces; in other words, so long as only these forms are present it is impossible to distinguish crystallographically whether the structure is characterized by holohedral symmetry or by diplohedral hemisymmetry.

Nos. 7 to 11 present faces of the tetrakis-hexahedron  $f(310)$ ; and it now becomes possible to determine whether the internal structure as shown by the external form is to be regarded as holohedral or hemihedral. As a matter of fact, in each of these crystals the faces of only one semiform  $\pi(310)$  are found to be present, the number varying with the more or less fractured state of the crystal. This combination is represented in fig. 3, from which, for the sake of simplicity, the small faces of the cube have been omitted. No. 7 presents all the twelve faces required by perfect hemisymmetry; No. 8 shows eight faces, No. 9 shows five, while on Nos. 10 and 11 only two are present; but on none of these crystals can any faces of the complementary semiform  $\pi(130)$  be distinguished.

Crystal No. 12 is five eighths of an inch ( $=1.6$  centim.) long, and projects from a matrix of quartz and mica. It is particularly interesting as showing the hemihedral development, not only of the above tetrakis-hexahedron, but also of an hexakis-octahedron having its planes in the edge-zones of the dodecahedron. The angle made by the faces of this new form with the adjacent faces of the form  $(211)$  was measured by help of the telescopic images to be  $10^{\circ} 48'$  in one case and  $11^{\circ} 2'$  in another; there is no doubt, then, that the faces belong to the semiform  $\pi(312)$ , for which the corresponding calculated angle is  $10^{\circ} 54'$ . Fig. 4 represents the actual development of the various faces on that part of the crystal

which is not concealed by the matrix: no fewer than ten faces of this semiform  $\pi(312)$  can be seen, while not a single face of the complementary semiform  $\pi(321)$  is to be found.

Gustav Rose has remarked that, in cases of diplohedral hemisymmetry, the poles of all the faces present belong in general to one set of systematic triangles: this crystal of Skutterudite forms another of the rare exceptions to this rule, which would require the association of  $\pi(321)$  instead of  $\pi(312)$  with the semiform  $\pi(310)$ .

This semiform  $\pi(312)$  is again to be observed on crystal No. 13, though it is there represented by only a single face. The angle with the adjacent face of the form  $(211)$  was in this case measured to be  $10^\circ 52\frac{1}{2}'$ , a result according well with the calculated angle  $10^\circ 54'$ : on the same crystal eight faces of the semiform  $\pi(310)$  are developed.

The last crystal, No. 14, differs from the rest in showing three faces, which, if the crystal were simple, would undoubtedly be attributed to the complementary semiform  $\pi(130)$ ; the crystal, however, still presents a hemihedral habit, since the three faces of this complementary semiform  $\pi(130)$  only appear at quoins where the faces of  $\pi(310)$  are missing. It is very possible indeed that the crystal may be twinned about the normal to a dodecahedron-face, as is at times the case in iron pyrites—which theory would likewise account for the presence of reentrant angles, otherwise to be attributed to parallel growth.

The subordinate forms  $(332)$ ,  $(643)$ , described by vom Rath, do not seem to be present on any of the above crystals, and must be very rare. In some cases indeed the edges of intersection of the octahedron with the form  $\pi(310)$  are "rounded off" by very small faces not susceptible of measurement; while the edges of the octahedron itself are bevelled by narrow planes, which, if crystal-faces at all, can only be approximately determined. On one crystal the angles made with the adjacent octahedral faces by the four tautozonal rudimentary planes of the triakisoctahedron were measured by the method of maximum illumination as  $18\frac{1}{2}^\circ$ ,  $17\frac{1}{4}^\circ$ ,  $13^\circ$ ,  $16\frac{1}{2}^\circ$  respectively—thus suggesting the form  $(221)$ , which requires an angle of  $15^\circ 48'$ , and, as we have seen, was given by Miller, no doubt in mistake, as an observed form. On another crystal a series of images could be obtained from each of two faces of the triakisoctahedron; and the limiting-values thus determined for the angle corresponding to the one just mentioned were, in one case  $13\frac{1}{2}^\circ$ – $16\frac{1}{4}^\circ$ , and in the other  $15\frac{3}{4}^\circ$ – $16\frac{1}{2}^\circ$ ; on a third crystal two similar angles were measured at  $15\frac{1}{4}^\circ$  and  $19^\circ$ , thus again indicating the form  $(221)$ .

The range of specific gravity of the crystallised mineral is a little wider than that of the massive as determined by Breithaupt: one crystal presenting no external sign of impurity was found to have a specific gravity of 6.48; a second had a specific gravity of 6.37, but, like the less dense specimens of Breithaupt, evidently contained foreign matter. Two other fairly large crystals had specific gravities of 6.56 and 6.72 respectively; while a small apparently very pure crystal, with smooth lustrous faces, gave a result as high as 6.86.

LXIII. *Action of Free Molecules on Radiant Heat, and its Conversion thereby into Sound.* By JOHN TYNDALL, F.R.S.

[Concluded from p. 462.]

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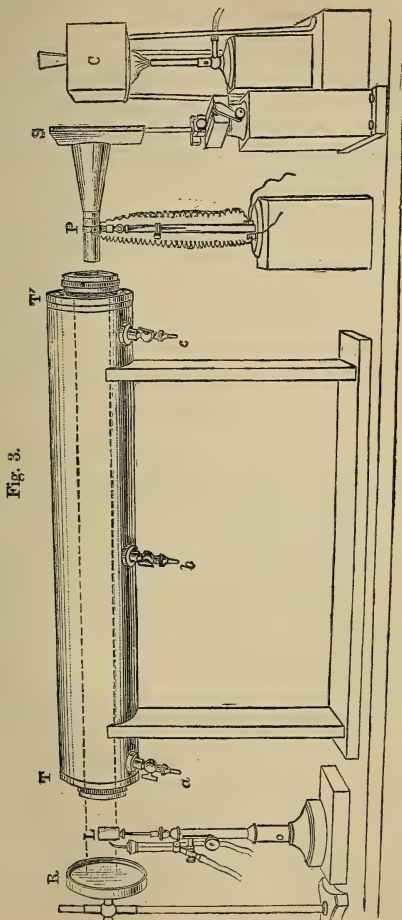
§ 5. *New Experiments. Hypothesis of Internal Films.*

*a. The Experimental Tube.*

I WISH now to come to closer quarters with the argument urged by Magnus and repeated by MM. Lecher and Pernter, namely that my results were due to "vapour-hesion"—that is to say, to liquid films condensed on my experimental tube and on my plates of rock-salt. The two investigators last named express unqualified surprise that I should have neglected the simple precaution of experimenting with blackened tubes. But this precaution was by no means neglected by me. I have repeatedly fortified myself by experiments of this character, with the result recorded in Table I. But I went further. A smooth coating of lampblack, however powerful as an absorber, might be competent to reflect a certain portion of the incident heat. Hence my desire to get entirely rid of reflection, by avoiding all contact with the interior surface of the experimental tube.

In fig. 3 an apparatus is sketched, by means of which this has been accomplished. T T' is a stout tube of brass, 36 inches long and 6 inches internal diameter. Projecting from

its otherwise closed ends are screws 1 inch each in depth, surrounding circular apertures  $3\frac{1}{8}$  inches in diameter. By means of screw-caps these apertures may be closed air-tight by trans-



parent plates of rock-salt, the plates being protected from crushing by washers of indiarubber. *a* is a cock leading to an air-pump and a barometer-tube; *b* is a cock to which flasks can be attached; while *c* is a cock connected with a purifying-apparatus (not shown). This consists of a U tube filled with fragments of clean glass moistened with sulphuric acid, and of a second tube filled with fragments of Carrara marble wetted with caustic potash. A plug of cotton-wool intercepts the floating matter of the air. The source of heat *L* is a cylinder of carefully prepared lime, against which a flame of coal-gas and oxygen impinges. The incandescent lime faces the concave mirror *R*, which receives the rays and sends them back in a parallel beam through the tube *T T'*. *P* is the thermopile, from which wires proceed to a distant galvanometer, the reflected dial of which is observed through a telescope. *S* is an adjusting-screen. At *C* is what, in my former researches, I have called the "compensating cube," used to neutralize the radiation from the source *L* and to bring the galvanometer-needle to zero. The chief object of this arrangement is to enable the experimenter to send a calorific beam along the axis of the tube *T T'* which shall never touch its internal surface. The great width of the tube, aided when necessary by diaphragms, renders this easy of accomplishment.

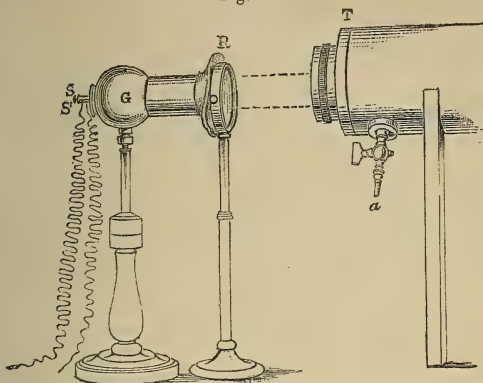
The mode of operation is readily understood. Suppose the heat impinging on the pile to produce a galvanometric deflection of  $50^{\circ}$ . This, the "total heat," is neutralized by the radiation from the compensating cube. To render the compensation accurate, the double screen *S* is shifted by an extremely fine screw-motion. Even when the total heat is very large it is possible, by means of this screen, to neutralize accurately the radiation of the source and bring the needle to zero. Suppose it to be there when the tube *T T'* is exhausted; on permitting a gas or vapour capable of absorbing radiant heat to enter *T T'*, the preexisting equilibrium is destroyed, the needle moves promptly away from zero, and from the observed deflection the absorption may be calculated.

Instead of the concave reflector, a rock-salt lens of great purity is sometimes used to render the beam parallel. When the lens is used, the incandescent portion of the cylinder of lime is caused to face the tube *T T'*, between which and the lime the lens is introduced. Instead of the incandescent lime, a spiral of platinum-wire heated to redness by a voltaic current is frequently employed as the source of heat. The spiral is placed in the centre of a brass globe *G*, fig. 4, and is connected with the screws *S S'* fixed in the back of the globe,



from which wires pass to the battery. R shows the position of the rock-salt lens, while one end of the experimental tube is shown at T. The greatest care is here necessary to protect the spiral from any agitation of the air. Such care, however,

Fig. 4.



it is always in the experimenter's power to bestow. To secure constancy in the radiation, the battery was charged three times a day, the strength of the current being regulated by a rheostat, and checked by a tangent-galvanometer.

An experimental tube of the description shown in fig. 3 was first employed by me about twelve years ago; and with it I then verified all the experiments I had previously made on the absorption of radiant heat by gases and vapours. The experiments were not published in any scientific journal; but they are thus referred to at page 394 of my volume of collected memoirs, entitled '*Contributions to Molecular Physics in the domain of Radiant Heat*:'—"The two ends of an experimental tube, 38 inches long and 6 inches in diameter, were each provided with an aperture 2.6 inches in diameter. These apertures were closed with plates of rock-salt. The source of heat was a platinum spiral, well defended from air-currents, and heated to redness by an electric current. In front of the spiral was a rock-salt lens, which sent a slightly convergent beam through the tube. Behind the most distant plate was formed a sharply-defined image of the spiral, its size being such that it was wholly embraced by the plate of salt. Here, then, was a beam of heat passing through an experimental

tube without coming into contact either with the surface of the tube itself, or with any coating or lining of that surface. With this apparatus all my old experiments on vapours have been frequently repeated. There is no substantial difference between the results thus obtained and those obtained with an experimental tube where nineteen twentieths of the heat which reached the pile was reflected heat."

The tube referred to in this extract was of rough brass, tarnished within. Hence, when air entered it, after exhaustion, the dynamic heating of the tube and the partial condensation of the vapour when the air was moist, produced an amount of radiation from its internal surface which, though small, was a source of some disturbance. In my present experiments, therefore, another tube, of the dimensions above given, is employed; and to reduce to a minimum any radiation from its internal surface, it is coated within with silver deposited electrolytically, and highly polished. Experiments with this tube show that it does not in any way disturb the true radiation from the source.

In Table I. are recorded five series of measurements executed with a brass tube polished within. But as the liquids, though reported pure by the manufacturing chemist, vary slightly from time to time, I thought it advisable to adhere to the same samples in experiments wherein a tube with reflecting interior is to be compared with one permitting of no reflection. The following five series of new measurements were therefore executed with the tube first mentioned.

TABLE III.

Brass tube with internal reflection.

	Pressures.	A Spiral dark.	B Spiral bright.	C Lime, free.	D Lime, mirror.	E Lime, lens.
Bisulphide of carbon . . . . .	·48	5·0	3·1	3·4	3·1	2·5
Chloroform . . . . .	·36	7·9	5·3	5·6	4·8	5·0
Benzol . . . . .	·32	9·6	8·6	7·9	6·9	6·3
Iodide of methyl . . . . .	·46	12·1	8·8	10·2	8·1	7·5
Iodide of ethyl . . . . .	·36	15·0	11·9	12·5	11·3	10·6
Amylene . . . . .	·26	21·9	15·6	16·0	14·4	12·5
Sulphuric ether . . . . .	·28	30·9	23·1	22·7	19·8	18·1
Acetic ether . . . . .	·29	36·9	27·3	29·6	24·1	...
Formic ether . . . . .	·36	...	...	29·6	25·0	23·8

Column A in this table contains the absorptions of the respective vapours, in hundredths of the total radiation, when the source was a platinum spiral just under incandescence, unaided by either lens or mirror. Under B are the absorptions when the source was the same spiral heated to bright redness.

The same vibrating atoms are preserved; but in A they vibrate on the whole more slowly than in B; and as the atomic periods of the transparent vapours synchronize best with the slower oscillations, the absorptions in A are considerably higher than those in B. Under C are the absorptions when the source was a moderate lime-light, produced by coal-gas and oxygen. Under D are the absorptions when the source was the lime-light with its heat gathered up and sent through the experimental tube by a concave mirror; while under E are the absorptions of the heat of the incandescent spiral aided by a rock-salt lens. The absorptions in D and E are somewhat less than those in C, because the path of the rays was diminished, through the reduction of internal reflection by the mirror and lens.

With the foregoing results, obtained with the brass experimental tube polished within, where the greater portion of the heat reaching the pile had undergone reflection, are now to be compared those obtained with the silvered tube, where internal reflection was wholly avoided.

TABLE IV.

Wide silvered tube with no reflection.

	L A Spiral dark.	L B Spiral bright.	M C Lime bright.	M D Lime moderate.	L E Lime dull red.
Bisulphide of carbon . . . . .	4.0	1.8	1.5	1.5	3.3
Chloroform . . . . .	5.6	3.0	3.5	4.3	6.0
Benzol . . . . .	7.0	5.1	4.4	6.5	8.0
Iodide of methyl . . . . .	7.5	5.9	5.0	6.5	9.2
Iodide of ethyl . . . . .	11.3	7.6	6.8	8.5	11.2
Amylene . . . . .	15.0	11.8	8.8	12.0	17.3
Sulphuric ether . . . . .	21.2	17.1	12.5	15.0	25.0
Acetic ether . . . . .	26.0	20.0	16.3	24.0	32.0
Formic ether . . . . .	27.0	21.0	17.0	25.0	34.0

The vapour-pressures here were those given in Table III. Column A contains the absorptions measured when the source of heat was a spiral under incandescence, aided by a rock-salt lens. B contains the absorptions measured with the same arrangement, the spiral being raised to bright redness. As usual, the heat of lowest refrangibility is most absorbed. C contains the absorptions of a tolerably intense lime-light aided by the silvered mirror; D the absorptions of the same light with its intensity reduced; while E contains the absorptions of the rays from a lime-cylinder heated to dull redness by a steady flame of hydrogen, burning in air, and aided by a rock-salt lens.

Here, then, where no trace of reflected heat is sent to the pile, we have substantially the same results as those obtained when by far the greater portion of the heat reaching the pile had undergone reflection. The agreement shows that the films, the action of which had been posited, but never proved, are, in regard to this action, what I always knew them to be, imaginary.

### b. *The Plates of Rock-salt.*

Having thus, I trust effectually, disposed of the hypothesis which ascribed my results to liquid layers covering the interior surface of the experimental tube, I proceed to the examination of the plates of rock-salt, which have also been credited with a liquid deposit. The hypothesis is to a great extent disposed of in a paper of mine published in the *Philosophical Transactions* for 1864, which, like other papers, has been overlooked by writers on this question. An apparatus is there described which enabled me to operate upon gaseous strata of different thicknesses, the thickness in each case being measured with great accuracy by aid of a vernier. Let two polished plates of rock-salt be supposed in close contact with each other, and let them be gradually separated by a suitable rack-and-pinion movement. From the first moment of their separation let the space between them be copiously supplied with vapour. Liquid films, if they form at all, will be deposited when the distance between the plates of salt is but small. As far as the films are concerned, they will be as influential when the plates are  $\frac{1}{20}$  of an inch apart as when they are 2 inches apart. Hence, if the hypothesis of my opponents be correct, the absorption ought to declare itself with the former amount of separation as clearly as with the latter. But if, as I allege, the absorption be the act of the vapour molecules, then the deepening of the vapour stratum will be accompanied by an increase of the absorption. The following experiment, bearing directly on this subject, was executed in 1864. My plates of salt were first fixed at a distance of  $\frac{1}{20}$  of an inch asunder; and the space between them was copiously supplied with air saturated with sulphuric-ether vapour. The distance between the plates of salt was then augmented by steps, as shown in the following table; and at each step the absorption was determined. Here are the results :—

Thickness of vapour stratum.	Absorption.
0·05 inch . . . . .	2·1 per cent.
0·1    " . . . . .	4·6    "
0·2    " . . . . .	8·7    "
0·4    " . . . . .	14·3   "
0·8    " . . . . .	21·0   "
1·5    " . . . . .	34·6   "
2·0    " . . . . .	35·1   "

We thus see that when the depth of the vapour stratum augments from  $\frac{1}{20}$  of an inch to 2 inches, the absorption augments from 2 per cent. to 35 per cent. of the total radiation.

It is only with sulphuric ether that an absorption of 2 per cent. by the thinnest stratum could be obtained. With most other vapours the action of a layer  $\frac{1}{20}$  of an inch in thickness proved insensible. We may thus begin with a layer which yields an absorption immeasurably small, gradually augment the thickness of the absorbing layer until it becomes a column 38 inches long, and find, throughout, the increase of absorption running hand in hand with the increase of the length of the absorbent layer. This result is utterly irreconcilable with the hypothesis that liquid layers on the plates of salt played any important part in my experiments.

With regard to "vapour-hesion," I have to make the following further remarks. Let a thin plate of polished rock-salt be placed upon, or against, the face of the thermopile, with its lampblack removed, so as to expose a clean metallic surface. Let an open glass tube end about a quarter of an inch above the plate of salt; and through this tube let a current of mixed air and vapour be gently urged downwards against the plate. No fine spray, which might readily arise from bubbling through a liquid, is to be permitted to mingle with the vapour. My vapours, I may say, have been usually formed, without bubbling, in large flasks, each containing a portion of a volatile liquid, the vapour of which was permitted to diffuse in the air of the flask. Fletcher's foot-bellows were employed to urge the vapours forward. The needle being at zero, or thereabouts, on causing the mixed current to impinge upon the rock-salt, the needle immediately swings aside, the deflection varying from  $20^{\circ}$  to  $80^{\circ}$  and more, according to the delicacy of the galvanometer and the quality of the vapour.

From such experiments, which prove heat to be liberated when vapour comes into contact with the salt, the condensation of the vapour has been inferred. I accept the inference.



This, however, does not imply the acceptance of the inference from this inference, that the condensed films exert the action ascribed to them on radiant heat. To test whether they do so or not, I had a circular plate of rock-salt mounted on its edge, and so placed that a beam of heat passed through it normally to a distant thermopile. The source of heat was an incandescent spiral, aided by a concave mirror; and the total radiation, after passing through the salt and impinging on the pile, produced a deflection of  $51^{\circ}$ . This radiation was accurately neutralized by a compensating cube, the needle under the operation of the two opposing forces pointing to  $0^{\circ}$ . By an arrangement which every experimenter can imagine for himself, sheets of air, laden with various vapours, could be poured in succession over the plate of salt. If, under these circumstances, absorbent films were formed, the equilibrium would be destroyed and the needle would move from  $0^{\circ}$ . My slit, which was the flattened base of an open tin cone, was placed across the upper part of the plate of rock-salt, so that the vapours, which were all heavier than air, should fall over the plate downwards. Here are the results obtained when the following vapours were permitted to form films upon the plate:—

Bisulphide of carbon . . . .	A barely sensible action.
Chloroform . . . . .	No action.
Benzol . . . . .	No action.
Iodide of methyl . . . . .	No action.
Iodide of ethyl . . . . .	No action.
Amylene . . . . .	No action.
Sulphuric ether . . . . .	A barely sensible action.
Acetic ether . . . . .	No action.
Formic ether . . . . .	No action.
Alcohol . . . . .	No action.

The minute deflections produced by bisulphide of carbon and sulphuric ether had nothing to do with liquid films; so that the words "no action" might have been written against these substances as against the others. While therefore recognizing the fact of condensation, these simple experiments prove how incorrect it is to credit the condensed films with the effects which have been ascribed to them. According to Magnus, alcohol exhibits a force of vapour-hesion particularly strong; but we here see that even this vapour produces no sensible effect. The vapours have been tested with other sources of heat, with the same result.

The deportment of dry and humid air is, as usual, very instructive. When the thin plate of rock-salt resting on the

naked face of the pile was exposed to the common air of the laboratory, it, of course, contracted a film corresponding to the humidity of the air. The sweeping away of this film by dry air produced a very small deflection indicating cold. When, on the contrary, humid air was urged against the salt, the deflection indicating heat was prompt and large. We have now to test the action of the liquid film thus formed upon radiant heat. The circular plate of rock-salt before referred to was mounted, with the incandescent spiral on one side and the pile on the other. The slit was so arranged that dry and humid air could be sent in succession over the surface of the plate. As before, the radiation from the spiral was neutralized by the compensating cube, the needle pointing to zero when the two sources were in equilibrium. On sweeping dry air over the plate of salt, so as to remove the film contracted from the laboratory air, there was no motion of the needle. On pouring humid air from the slit over the salt, there was no motion of the needle. To moisten the air it was urged from bottom to top through a tall jar filled with wet bibulous paper. The same apparatus had furnished humid air which produced a swing of  $80^{\circ}$  when urged against the thin plate of rock-salt resting on the face of the pile. As a barrier to radiant heat it was nevertheless powerless. The condensation may even be considerably enhanced without producing any sensible effect. Through a glass tube I urged my breath against the plate of salt so as to produce the colours of thin plates, without any sensible effect upon the galvanometer.

Having thus clearly shown what films, even in an exaggerated form, cannot accomplish, I hope, in testing the action of humid air, that the use of the silvered tube, closed with polished plates of rock-salt, on which no trace of visible moisture is deposited, will be conceded to me. This tube involves the use of a source of heat of small dimensions. The lime-light, though fulfilling this condition, is not suitable, because of the high refrangibility of its heat. The incandescent platinum spiral would be better; still the radiation from this source is but feebly absorbed by the aqueous vapour taken up by air at ordinary temperatures. The oxyhydrogen flame fulfils the required conditions best\*. It has the advantage of high temperature and low refrangibility; while the fact

\* I was careful to assure myself that, unless it amounted to the visible wetting of the plates of salt, there was no sensible stoppage of the rays from the oxyhydrogen flame. This quite agrees with the result obtained by Magnus himself, in the experiment with the concave mirror already referred to. Unless he visibly wetted the mirror, he failed to impair the energy of the reflected beam.

that its heat, as coming from aqueous vapour, is absorbed with special energy by aqueous vapour, is also a strong recommendation. In the Bakerian Lecture for 1864 I have illustrated this point. It was then shown that when a platinum spiral, rendered incandescent by a voltaic current, had 5·8 per cent. of its heat absorbed by undried air, a hydrogen-flame had from 17 to 20 per cent. of its heat absorbed. The mere plunging of a platinum spiral into the flame caused the absorption to fall from 17 per cent. to 8·6 per cent. Hence my reason for choosing a hydrogen-flame in the present instance.

Dry air and humid air being caused to occupy the experimental tube in succession, both of them were compared with the radiation through the tube when very perfectly exhausted by a Bianchi's pump. The following results were obtained:—

	Deflection.	Absorption per 100.
Vacuum . . . . .	0°·0	0·0
Dry air . . . . .	0°·0	0·0
Humid air . . . . .	8°·0	11·7
Vacuum . . . . .	0°·0	0·0
Dry air . . . . .	0°·0	0·0
Humid air . . . . .	7°·6	11·2

The deflection through a vacuum, otherwise the total heat, was 47°, which, according to my calibration-table, is equivalent to 68 units.

A fresh supply of hydrogen was here introduced into the gas-holder. The total heat being 46° or 65 units, the following results were obtained:—

	Deflection.	Absorption per 100.
Dry air . . . . .	0°·0	0·0
Humid air . . . . .	6°·2	9·5
Dry air . . . . .	0°·0	0·0
Humid air . . . . .	6°·7	10·3

Mean of the four determinations with humid air, 10·7.

A column of humid air 38 inches long absorbs, according to these experiments, 10·7 per cent. of the radiation from a hydrogen-flame. I have been criticised for estimating the absorption of the earth's rays within 10 feet of the earth's surface at 10 per cent. This estimate I consider a moderate one; and the foregoing experiments prove it to be so.

It would be an error to suppose that determinations like these are easily made. They require the most scrupulous care for their successful accomplishment. The hydrogen issued

from the gas-holder through an orifice of fixed dimensions in a stream of the utmost possible constancy. It was then led into a Sugg's regulator, whence it issued under an absolutely constant pressure. The flame issued from a circular brass burner with an aperture  $\frac{3}{16}$  of an inch in diameter. It was carefully surrounded by a hoarding, the space within the hoarding being packed with horsehair. Every precaution in fact was taken to avoid the agitation of the air around the flame. Proper care was also taken to secure the pile against disturbance by air-currents. The air being first purified, by passing it through caustic potash and sulphuric acid, was rendered humid by carrying it over wet bibulous paper contained in a suitable tube. It required some minutes to enter; and it was therefore necessary, by prior patient observance of the needle, to make sure that during this interval no change occurred in the radiation save that effected by the humid air itself. The humid air was removed from the experimental tube, not by exhaustion (which always causes precipitation), but by gently forcing, by means of a compressing-pump, dry air through the tube. When this was done, the needle, in all the experiments above recorded, returned within a small fraction of a degree to zero\*.

With the rough, wide experimental tube to which reference has already been made, I, ten years ago, found the absorption of a column of humid air 38 inches long to be 8 per cent. of the total radiation from a flame of hydrogen.

### § 6. *Conservation of Molecular Action.*

If the absorption of radiant heat be the act of the constituent atoms of compound molecules, its amount depending solely on the number of molecules encountered by the calorific waves, then, whatever may be the changes of density which gases and vapours undergo, so long as the number of molecules remains the same, the absorption ought to continue constant. Such constancy, should it be proved to exist, I name the "conservation of molecular action." The experiments now to be described deal with this question.

Besides the silvered experimental tube already described as 38 inches long, I had another constructed of the same diameter, and with similar terminal apertures. Its length was 10·8 inches. The one tube was, therefore, 3·5 times the length of the other. The shorter tube was constructed with the view of proving that the absorptions I had recorded in previous

\* The temperature of the laboratory air during the foregoing experiments was 60° Fahr.

memoirs were exerted by the vapour molecules, and not by liquid layers deposited on my plates of salt. The hypothesis of such layers, however, being completely disposed of, we can carry the experiments a step further. Assuming that the absorption does not change with change of density, so long as the quantity remains constant, it would follow that 1 mercury inch of vapour in the long tube ought to quench as much heat as 3·5 inches in the short one. The same conclusion ought, of course, to hold good when we compare 2 inches of vapour in the long tube with 7 inches in the short one.

The experiments have been made, and with the following results:—

*Sulphuric-ether vapour.*

Short experimental tube.

Pressure.	Deflection.	Absorption per 100.
3·5 inches . .	24°	30
7       " . .	30	37·5
Total heat .	50	

Again,

3·5 inches . .	24°	30
7       " . .	31·5	39·4
Total heat .	50	

Taking the means of these two experiments, we have the absorptions—

For 3·5 inches . . . . . 30 per cent.

For 7       " . . . . . 38·5   "

Such is the result obtained with the short tube. We now turn to the long one:—

Long experimental tube.

Pressure.	Deflection.	Absorption per cent.
1 inch . . . .	23°	30·3
Total heat .	49	
2 inches . . .	31	38·8
Total heat .	50	

These results are almost identical with those obtained with the short tube and greater pressures.

The source of heat in this case was a dull lime-light. In subsequent experiments the light was brightened. Here is the result:—

Long experimental tube.

Pressure.	Absorption.
1 inch . . . . .	22·3 per cent.
2 inches . . . . .	29·5   "



Short experimental tube.

Pressure.	Absorption.
3·5 inches . . . . .	22·5 per cent.
7·0 „ . . . . .	30·0 „

The agreement here is almost as close as that established by the first experiment.

With a still brighter source of heat the absorptions were:—

Long tube.

Pressure.	Absorption.
1 inch . . . . .	18·4 per cent.
2 inches . . . . .	25·7 „

Short tube.

3·5 inches . . . . .	18·8 per cent.
7·0 inches . . . . .	25·6 „

When, therefore, the density of the vapour varies inversely as the length of it traversed by the calorific rays, the absorption remains constant.

The hydride of amyl lends itself conveniently to experiments of this character. With it, and with the lime-light as source, the following measurements have been made:—

*Hydride of amyl.*

Long experimental tube.

Pressure.	Deflection.	Absorption.
1 inch . . . . .	10°	12·8
2 inches . . . . .	15	19·2
Total heat .	49·4	

Short experimental tube.

Pressure.	Deflection.	Absorption.
3·5 inches . . . . .	10°	12·2
7·0 „ . . . . .	15	18·3
Total heat .	50·5	

The agreement here is close enough to illustrate the law, the greatest difference being under 1 per cent.

At this point the following entry appears in my note-book:—  
 “It might have been wise on my part to rest content with the comparison of the long and short tubes with the lime-light as source of heat. But for the sake of completeness I wished to introduce the incandescent spiral. The fulfilment of this wish—that is to say, the successful performance of a single experiment—has cost me more than a week’s work. Once, however, committed to the task, I could not leave it incomplete.

"The discrepancy between the two tubes was in no case great, hardly ever exceeding 2 per cent. But the difference was uniformly in favour of the long tube and small density. Diaphragms were employed; the position of the short tube was shifted; and it was finally placed so that the pile should occupy the same position in relation to its adjacent end as it did in relation to the adjacent end of the long tube. The discrepancies then disappeared, the absorptions in the two tubes proving practically identical.

"Many leaves of paper were covered with observations during the week; but it is useless to take up time and space in copying them here. One representative observation will suffice."

*Sulphuric ether.*

Source of heat—bright-red spiral with rock-salt lens.

Long experimental tube.

Pressure.	Deflection.	Absorption.
1 inch . . . . .	20°·0	23·5
2 inches . . . . .	27°·3	32·1
Total heat .	51°·0	

Short experimental tube.

Pressure.	Deflection.	Absorption.
3·5 inches . . . . .	17°·8	23·4
7·0 " . . . . .	24°·8	32·6
Total heat .	49°·0	

The agreement between the two tubes is as perfect as could be desired.

It is easy to record these experiments; but it is not so easy to make them. On every portion of the apparatus (the source, the tube, the thermopile, and the galvanometer) extraordinary care must be bestowed to make the experiments strictly comparable. The results were checked by taking the total heat after every experiment—a precaution which ensured the detection of any variation on the part of the source. When the platinum spiral was used, the battery of ten Grove's cells, employed to render it incandescent, had to be very carefully prepared, freshly amalgamated zinc plates being used in each fresh battery. The requisite deflection of a tangent compass being produced, it was kept constant by means of a rheochord throughout the day. When the battery showed signs of rapid falling, it was always renewed. It would be tedious to dwell upon the precautions taken to protect the source and the pile from the least agitation of the air. Such precautions are essential; but their necessity and form must be learnt by each experimenter for himself.

§ 7. *Thermal Continuity of Liquids and Vapours.*

I have amply illustrated by experiments, recently made, the correspondence which subsists between vapour absorption and liquid absorption, when the quantities of matter traversed in the two cases by the calorific rays are proportional to each other. This correspondence, as I have already stated, was established eighteen years ago. And though the result goes to the very core of the discussion which my researches have aroused, though in relation to that discussion they had, in my estimation, a weight and import greater than those of any other experiments published by me, they seem never for a moment to have attracted the attention of those who have taken part in the discussion. Here is the result, published in 1864, which illustrates the point now under consideration :—

Absorption per 100.			
		Vapour.	Liquid.
Bisulphide of carbon	0.48	4.3	8.4
Chloroform	0.36	6.6	25.0
Iodide of methyl.	0.46	10.2	46.5
Iodide of ethyl	0.36	15.0	50.7
Benzol	0.32	16.8	55.7
Amylene	0.26	19.0	65.2
Sulphuric ether	0.28	21.5	73.5
Acetic ether	0.29	22.2	74.0
Formic ether	0.36	22.5	76.3
Alcohol	0.50	22.7	78.6

The magnitude of the absorption in the liquids is far greater than in the vapours, because the quantity of absorbent matter is far greater in the former than in the latter ; but the order of absorption is the same.

When the vapours are doubled in quantity, the absorptions are considerably increased. When trebled they are still further augmented ; in other words, they approach more and more in magnitude to the absorptions of the liquids ; but the harmony as regards order is never disturbed. What, then, would occur if the vapours were so increased as to render the quantities of matter in the two states, not proportional, but *equal* to one another ? This is the question with which I now propose to deal. At the time when the results above recorded were obtained, I thought it probable that if a circular liquid layer of a given diameter could be vaporized in a tube of the same diameter, the absorption would remain unchanged. In other words, I thought that the liberation of the molecules from liquid cohesion would neither augment nor diminish their

action upon radiant heat. Since 1864 this problem has been often in my mind. The wide silvered tube, I am happy to say, has rendered the solution of the problem possible.

It is only highly volatile liquids that lend themselves to this experiment, because from them alone can vapours be derived of sufficient density to produce liquid layers of practicable thickness. On the 22nd of last October the experiment was first attempted. The source of heat was the lime-light, the rays of which were received by a concave mirror silvered in front, and sent in a nearly parallel beam through the experimental tube. At the end nearest the source the tube was provided with a diaphragm having a circular orifice 1 inch in diameter. At the other end was a diaphragm with an orifice  $\frac{1}{2}$  an inch in diameter. Beyond this was placed the thermopile, furnished, not with its reflecting cone, but with a tube of brass (shown in fig. 3) 2 inches long and blackened within. In this arrangement, the heat which reached the pile did not even approach the interior cylindrical surface. The total heat employed produced a deflection of 60 galvanometric degrees, which, when the tube was exhausted by a powerful Bianchi's air-pump, was accurately neutralized by a compensating cube. Liquid sulphuric ether was then placed in a large flask provided with a sound stopcock, the object being to expose a considerable evaporating surface. The flask was plunged in water, with the view of keeping the liquid and its vapour at an approximately constant temperature. The air being carefully removed from the flask, it was attached to the experimental tube, and a quantity of vapour was allowed to enter sufficient to render a column 38 inches long equivalent to a liquid layer 1 millimetre in thickness. Two concurrent experiments made the deflection produced by the vapour

41°.

Without altering the quality of the heat, the absorption exercised by a liquid layer of sulphuric ether 1 millimetre thick was next determined. The rock-salt cell with which the experiment was made is described in detail in the Bakerian Lecture for 1864 (Phil. Trans. vol. 154. p. 328.) The annexed figure (fig. 5) will give a sufficiently clear notion of its construction and disposition. Between two stout plates of brass, *c c* and its fellow, two rock-salt plates of extreme purity are firmly clasped by suitable screws, due care being taken to protect the plates from a crushing pressure. The two brass plates referred to are perforated by circular apertures, as shown in the figure. The two plates of salt are not allowed to come into contact, but are separated from each other by a carefully

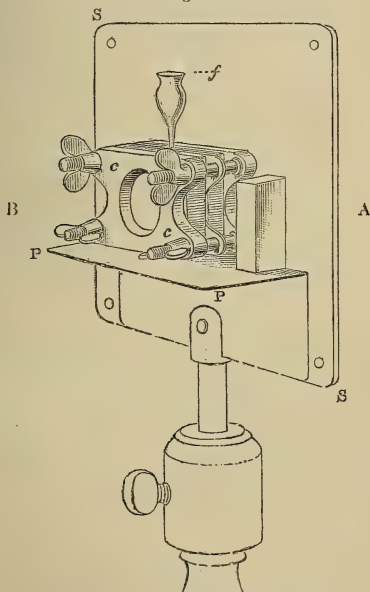
worked brass plate 1 millimetre thick, perforated like *c c*. A portion of this middle plate is cut away, opening a passage into the interior of the cell. Through this passage the cell is filled with liquid by means of the funnel *f*. The cell is placed on a platform *P P* riveted onto the double brass screen *S S*. The source was placed at *A*, and the thermopile with its blackened tube at *B*. It is not necessary to figure them.

The needle being brought accurately to zero by the compensating-cube when the cell was empty, liquid sulphuric ether was poured in. The consequent deflection was

42°.

Here vapour absorption and liquid absorption were so nearly alike as to stimulate me to further efforts. The entry in my

Fig. 5.



note-book on the 22nd ends with the remark :—" I purpose repeating this experiment on Monday, with the view of rendering the result secure."



On Monday, accordingly, the experiments were resumed; but they proved by no means so easy as I had hoped to find them. For five days I worked at the subject without coming to any satisfactory conclusion. The source, the mirror, the cell, the experimental tube, and the thermopile were all in turn objects of scrutiny; but there still remained a difference between the action of the liquid and that of its vapour sufficient to throw doubt on the assertion of their identity.

At the conclusion of many trials and precautions I found the absorption of the vapour still distinctly in excess of that of the liquid. I had reduced the spherical aberration to a minimum, by confining the reflection to a small central area of the silvered mirror. Still the image of the incandescent lime, formed at the end T' of the experimental tube, was large enough to encroach a little on the annular space surrounding the aperture closed by the plate of rock-salt. Diaphragms of polished metal had also been used, to lessen the amount of heat falling upon the pile. I figured to myself the heat impinging on the annular space and diaphragm, reverberated back to the end T of the experimental tube, reflected from the annular space and diaphragm at that end, and thus in part sent back to the pile. Such heat, instead of passing once through the vapour, would pass through it three times; and if it formed a sensible part of the total heat, might make vapour absorption appear greater than liquid absorption. I had the tube dismounted, and the annular spaces and diaphragms carefully coated with lampblack. Remounting the tube and measuring once more the vapour absorption, it was found to be

32.4 per cent.

This was the mean of five concurrent series of observations, in which every care was taken to ensure exactitude. Lest the total heat should vary during the execution of a series, it was taken at the conclusion of every individual experiment.

The absorption of sulphuric ether, acting as a liquid, was next determined. The mean of three series of experiments, two of which yielded identical results, and the third of which differed only 0.7 per cent. from the others, made the absorption of the liquid ether to be

32.9 per cent.,

which, I need not say, is surprisingly close to the vapour absorption, differing therefrom by only 0.5 per cent.

Informed by experiment that the heat from the incandescent platinum spiral was more powerfully absorbed than that of the lime-light, I thought it worth while to inquire whether the

liquid followed its vapour in absorptive energy when the quality of the heat was changed. On Monday the 31st, accordingly, the rays from the spiral being rendered parallel by a rock-salt lens, the absorption of sulphuric ether was determined, and found to be

66·7 per cent.;

while the absorption of the liquid was

67·2 per cent.,

which again gives a difference of only 0·5 per cent.

On another occasion I found the absorption by sulphuric ether to be :—

Vapour . . . . 71 per cent.

Liquid . . . . 70 „

On the 1st November I checked the result obtained with the lime-light and mirror, by using the lime-light and rock-salt lens. Here are the absorptions of the vapour and liquid respectively :—

Vapour . . . . 33·3 per cent.

Liquid . . . . 33·3 „

The absorptions are identical ; while the result agrees closely with that obtained with the concave reflector.

When the requisite quantity of sulphuric-ether vapour, viz. 7·2 mercury inches, was in the experimental tube, I tried whether the radiation from a Leslie's cube, coated with lamp-black and filled with boiling water, could pass through the vapour. About 14 per cent. of the incident heat was transmitted. Had I been asked at the time whether a liquid layer of sulphuric ether 1 millimetre thick was pervious to the heat of the cube, I should have replied with some confidence in the negative. Hence, for the moment, I thought the experiment opposed to the law that vapour absorption and liquid absorption, when equal quantities of matter are compared, are the same. On actually testing a layer of the liquid ether 1 millimetre thick, the transmission of upwards of 6 per cent. of the incident heat was observed. So that in this case also we have harmony of deportment between liquid and vapour. The absorption of the vapour exceeds that of the liquid, because the heat from the cube radiated freely against the interior silvered surface of the experimental tube, and by its reflection from that surface had its path through the vapour augmented in length. This augmentation naturally carried with it an increase of the absorption.

The next substance examined was hydride of amyl, the boiling-point of which is 30° Fahr., or 5° lower than that of

sulphuric ether. When a large evaporating-surface is exposed, there is therefore no difficulty in obtaining, from this liquid, vapour of a pressure of 6.6 inches of mercury. This, in a tube 38 inches long, would, if squeezed to liquefaction, produce a layer 1 millimetre thick. Vapour absorption and liquid absorption being measured in succession, this is the behaviour of the hydride of amyl:—

Absorption by vapour . . . .	51 per cent.
Absorption by liquid . . . .	51 „

the two absorptions being absolutely identical\*.

Combining this section and the last, their joint results may be thus summed up. Beginning with a column of sulphuric-ether vapour 38 inches long at 7.2 inches pressure, or with a column of hydride-of-amyl vapour 38 inches long and at 6.6 inches pressure, and gradually shortening the column without altering the quantity, the vapour would gradually augment in density and pass wholly, when reduced to a thickness of 1 millimetre, into the liquid state of aggregation. Suppose a beam of heat of constant value, after passing through the vapour, to impinge upon a thermopile and to produce a definite galvanometric deflection; this deflection would remain absolutely fixed during all the changes of density and aggregation which we have supposed the vapour to undergo. In other words—as regards the absorption of radiant heat, the vapour would pass, without breach of continuity, through all its stages of condensation into the liquid form of matter.

A general law of molecular physics is, I apprehend, here illustrated.

#### § 8. *Rhythmic Absorption of Radiant Heat by Gases and Vapours.*

Conclusive as the foregoing experimental argument must appear as regards the action of free molecules upon radiant heat, I am nevertheless glad to supplement it by another of a totally different character. On the 29th of November, 1880, I had the pleasure of witnessing, in the laboratory of the

\* When the rock-salt cell was empty, reflection of course occurred at its two interior surfaces. A perfectly diathermanous liquid, with the refractive index of rock-salt, would annul this reflection. And though the liquids actually employed had a smaller refractive index than rock-salt, and though they were far from being perfectly diathermanous, their introduction into the cell must nevertheless have diminished the reflection, and thus added to the transmitted heat. This addition, having been determined by calculation, was sensibly neutralized by the introduction of washers of thin note-paper, which slightly augmented the thickness of the liquid stratum traversed by the calorific rays.

Royal Institution, the remarkable experiments of Prof. Graham Bell, wherein musical sounds were evoked by causing an intermittent beam of light to impinge upon thin disks of various kinds of matter. I was soon convinced that the effects were due to the rhythmic gain and loss of heat. Being occupied with experiments on gases and vapours at the time, I thought that they might be invoked to decide the nature of the action revealed by Prof. Bell. The result was mentally clear before the experiment was made. I pictured a highly absorbent vapour, exposed to the shocks of the intermittent beam, suddenly expanding during the moment of exposure, and as suddenly contracting when the beam was intercepted. Pulses of an amplitude probably far greater than those obtainable with solids would, I thought, be thus produced; and these pulses, if caused to succeed each other with sufficient rapidity, would be sure to produce musical sounds.

This idea was tested and verified on the spot. The 'Journal of Telegraph Engineers' for December 8th, 1880, contains the following record of what occurred:—"When Professor Bell was good enough to show me his experiments, I happened to be myself experimenting on the action of vapours upon radiant heat. Old experiments had revealed, and new ones had confirmed, the fact that, as regards the absorption of heat, there existed vast differences between vapours. This is well illustrated by the deportment of bisulphide of carbon and of sulphuric ether, one of which is highly transparent, and the other highly opaque to radiant heat. It occurred to me that, if the action were due to the absorption of heat, we might possibly extract musical sounds from sulphuric-ether vapour; whereas bisulphide-of-carbon vapour being transparent to heat-rays, they would for the most part go through this vapour unabsorbed, and produce no sonorous effect. I think Prof. Bell will bear me witness as to the result. We placed a quantity of sulphuric-ether vapour in a test-tube, and allowed an intermittent beam of light to strike upon the vapour far above the liquid, and we heard distinctly a musical tone of a pitch corresponding to the rapidity of the flashes. We then took the bisulphide-of-carbon vapour, and tried it in a similar manner, but neither Prof. Bell nor myself could hear any trace of a musical sound"\*.

\* Mr. Bell has given a perfectly accurate account of this occurrence in the *Philosophical Magazine*, vol. xi. p. 519. With reference to what occurred on the 29th of November he writes thus:—"Professor Tyndall at once expressed the opinion that the sounds were due to rapid changes of temperature in the body submitted to the action of the beam. Finding that no experiments had been made at that time to test the sonorous properties of different gases, he suggested filling one test-tube with the

It was obvious, however, that the arrangement of Prof. Bell—a truly beautiful one—was not suited to bring out the maximum effect. He had employed a series of glass lenses to concentrate his beam; and these, however pure, would, in the case of transparent gases, absorb a large portion of the rays most influential in producing sound. This may be illustrated by comparing a rock-salt lens, in my collection, with a glass lens of the same focal length prepared in the workshop of M. Duboseq. Transmitted through the former, the radiation from an incandescent platinum spiral produced a galvanometric deflection of  $55^\circ$ , possessing, according to the table of calibration, a value of more than 100. Transmitted through the latter, the deflection fell to  $10^\circ$ , or to less than  $\frac{1}{10}$  of the radiation transmitted by the rock-salt. The  $\frac{1}{10}$  here shown to be intercepted by the transparent glass, consist of heat on which transparent gases and vapours would exert a specially absorbent power. Hence the desirability of maintaining this important factor, in the radiation employed to test the sonorous power of such substances.

It was with the view of preserving intact these powerful calorific rays that I employed in my experiments on calorescence\* small concave mirrors silvered in front; and to these mirrors I now resorted. My more intense sources of heat comprised a Siemens lamp connected with a dynamo-machine; an ordinary electric lamp connected with a voltaic battery; and a lime-light, produced sometimes by the combustion of oxygen and hydrogen, and sometimes by oxygen and coal-gas. The lime-light (which was used by me in 1859) is so handy, steady, and otherwise effective, that I have applied it almost exclusively throughout this part of the inquiry. Sources of heat, however, of much lower temperature than the lime-light have proved competent to evoke musical sounds. A candle-flame, a red-hot coal, a red-hot poker, the same poker at the temperature of boiling water, and an incandescent platinum spiral have all been proved effective, though of course far less so than the concentrated lime-light†.

To produce the required intermittence, I first employed a circle of sheet zinc, 16 inches in diameter, provided with radial slits. This was afterwards exchanged for a second disk of the

vapour of sulphuric ether (a good absorbent of heat), and another with the vapour of bisulphide of carbon (a poor absorbent); and he predicted that, if any sound was heard, it would be louder in the former case than in the latter. The experiment was immediately made; and the result verified the prediction."

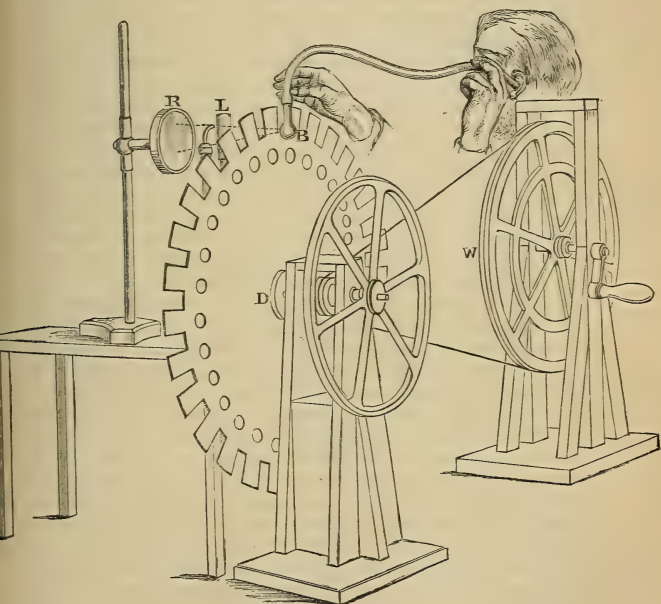
\* Philosophical Transactions, 1866, vol. clvi. p. 1.

† These earlier experiments will be found recorded in the Proceedings of the Royal Society, vol. xxxi. pp. 307, 478.



same diameter, but furnished with circumferential teeth and interspaces. The disk was mounted vertically on a whirling table, and caused to rotate across the beam near the focus of the concave mirror. Immediately behind the disk was placed the flask containing the gas or vapour to be examined, while an india-rubber tube, ending in a hollow cone of ivory or box-wood, connected the flask with the ear. With this arrangement, simple as it is, sounds of surprising intensity were obtained with all those gases and vapours which my previous experiments with the experimental tube and thermopile had proved to be powerful absorbers of radiant heat. The final arrangement was that shown in fig. 6.

Fig. 6.



The source of heat is the carefully worked and centred lime-cylinder L, heated by the oxyhydrogen flame. The rays from this source are received by the concave mirror R, and converged upon the bulb B, which contains the substance

to be tested. The bulb is connected with the ear by a piece of india-rubber tubing, ending in a tapering tube of boxwood or ivory. The intermittence of the calorific beam is effected by the disk D of strong cardboard, 2 feet in diameter, and provided at the circumference with 29 teeth and corresponding interspaces\*. The disk is caused to rotate by the wheel W, with which it is connected by a band. The positions of the sonorous bulb and of its ear-tube are shown in the figure. In the case of gases lighter than air, the bulb B is turned upside down. With the heavier gases it is held erect. When vapours are tested, a small quantity of liquid is poured into the bulb, which is shaken so as to diffuse the vapour in the air above the liquid. The bulb is held so that the point of maximum concentration of the beam falls upon it.

With this apparatus I have tested more than once the sounding-power of ten gases and of about eighty vapours. As a sound-producer chloride of methyl is supreme. It is, however, closely followed by aldehyde, olefiant gas, and sulphuric ether, the two latter being very nearly equal to each other. The volatility of the liquid from which the vapour is derived is of course an important factor in the result. For however high the inherent capacity of the molecule as an absorber may be, if the molecules be scanty in number the effect is small. Feeble vapours, on the other hand, may to some extent atone by quantity for the inherent weakness of their molecules. A few examples will suffice to show how the specific action of the molecules overrides the effect of volatility. Bisulphide of carbon, with a boiling-point of  $43^{\circ}$  C., is less powerful than acetic ether, with a boiling-point of  $74^{\circ}$ . Tetrachloride of carbon boils at  $77^{\circ}$ ; but its sound by no means equals that of acetal, which boils at  $104^{\circ}$ . Chloroform, with a boiling-point of  $61^{\circ}$ , is less powerful as a sound-producer than valeral, with a boiling-point of  $100^{\circ}$ , or even than valerianic ether, with a boiling-point of  $144^{\circ}$ . Cyanide of methyl boils at  $82^{\circ}$ —but produces less sound than acetate of propyl, with a boiling-point of  $102^{\circ}$ . In the experimental tube these vapours follow, as absorbers, the order of their sounds. When tested in liquid layers they follow the same order. I have examined about a score of liquids with boiling-points varying from  $163^{\circ}$  to  $308^{\circ}$ . At ordinary temperatures the vapours of these liquids were practically inaudible; the liquids being plunged in a bath of heated oil the vapours so produced emitted, for the most part, powerful sounds. The

\* Intermittence is sometimes produced by the series of equidistant circular apertures shown in the figure.

measured absorptions of a sufficient number of substances, in relation to their sounding-power, shall be tabulated immediately.

The fact is worth a passing reference, that the chlorides of the elements appear one and all to be feeble sound-producers, because they are one and all feeble absorbers of radiant heat. Many years ago I had found them highly diathermanous, and accepted chloride of sodium as representative of the class. Silicium chloride, for example, though very volatile, is weak as a sound-producer. Tetrachloride of carbon and terchloride of phosphorus are also volatile, but not strong. Bichloride of tin, chloride of arsenic, chloride of titanium, and chloride of sulphur are all feeble sound-producers. In these three cases the boiling-points are high: but non-volatility is not the cause of the weakness; for when the vapours are raised, by heating their liquids, almost to the pressure of the atmosphere, they are still but feebly sonorous. Whatever, then, the condition may be which renders these substances pervious to radiant heat, it appears to be a condition common to them all.

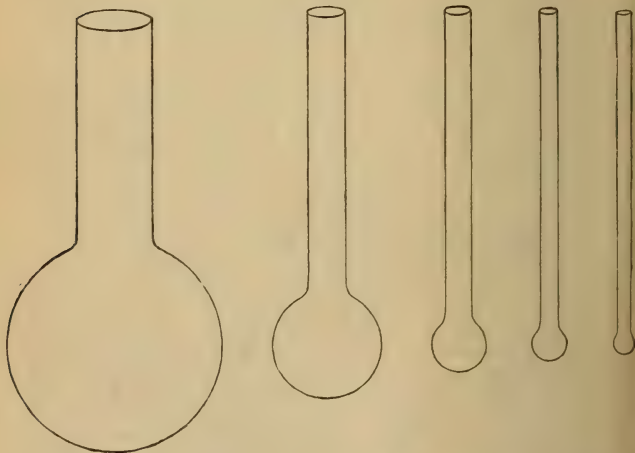
In experiments with the chlorides care must be taken to abolish all fumes. Bichloride of tin sounds loudly with fumes, but is weak without them. Simply heating the upper part of the flask frequently suffices to lower the sounds from loudness almost to silence.

The universality of its presence, and the discussions which it has provoked, rendered the action of water-vapour especially interesting to me. I did not imagine at the outset that the modicum of vapour diffused in atmospheric air at ordinary temperatures could produce sonorous pulses of sensible intensity. In my first experiment, therefore, I warmed water in a flask nearly to its boiling-point. I heated the flask above the water with the spirit-lamp flame, thus dissipating every trace of haze, and then exposed the clear vapour to the intermittent beam. The experiment was a virtual question put to the vapour as to whether I was right or wrong in ascribing to it the power of absorbing radiant heat. The vapour answered by emitting a musical note which, when properly converged upon the tympanum, seemed as loud as the peal of an organ. When the temperature was lowered from  $100^{\circ}$  C. to  $10^{\circ}$  C., the sound did not vanish, as I expected it would. It remained not only distinct but strong. The flasks employed in these experiments were dried in a variety of ways, of which I have already given some account, and which will suggest themselves to every experimenter in this field. Taken open from the laboratory, and exposed to the intermittent beam, the flasks are always to some extent sonorous. Placed beside

sulphuric acid underneath the receiver of an air-pump, and permitted to dry there, they are reduced to silence. The slightest invasion of humid air renders them again sonorous. Breathing for a moment into a dried and silent flask, a loud sounding-power is immediately manifested.

Flasks without lips have been specially blown for these experiments, the india-rubber tubing being readily pushed over their necks. Large flasks are not the most suitable. To produce effective pulses, sudden and intense expansions and contractions are required; and these are best obtained when the beam, at its place of maximum concentration, covers a large portion of the matter in the flask. Thin bulbs about a cubic inch in volume are both handy and effective; but the bulb may be reduced to  $\frac{1}{50}$ , or even  $\frac{1}{100}$ , of a cubic inch without rendering the sound insensible. A speck of water introduced into such tiny bulbs, when vaporized by heat, produces sounds which are not only sensible, but loud. A series of bulbs which I have actually employed in my experiments are represented in their natural dimensions in fig. 7.

Fig. 7.



It cannot be necessary to state that the absorption which produces the pulses is direct and immediate, being the act of the gaseous molecules. The pulses are not due to the heating of the glass envelope and the communication of its heat to

what it contains; for, were this the mode of heating, air would be as sonorous as olefiant gas. Nor are the pulses due to the sudden vaporization of a liquid layer which might be supposed to overspread the interior of the flask. When water at a low temperature is purposely caused to cover the interior surface, exposure to the beam produces sound of a certain intensity. When the flask is so heated in a spirit-flame as to chase away every trace of the adherent liquid, the exposure of the pure vapour, then within the flask, to the beam, generates a sound far louder than that produced when the liquid film was there. Holding the bulb containing the hot vapour for a little time in the intermittent beam, its temperature falls, the quantity of vapour diminishes, and the sound sinks in intensity. On quitting the spirit-flame, the bulb in some cases must have been near a red heat; but even at this temperature the vapour sounded loud.

It has, I think, been amply shown that when the molecules of a liquid are rendered free by vaporization they carry with them their absorbent power, liquids and vapours being pervious and impervious to the same quality of heat. Hence the inference, that prior transmission through a liquid of sufficient thickness ought so to sift a calorific beam as to render it powerless to act on the vapour of that liquid. Even with the loudest-sounding vapours this proves to be the case, a layer of liquid  $\frac{1}{8}$  of an inch thick being found generally sufficient to deprive the beam of its efficient rays, and the vapour of its sounding-power.

In transparent liquids, the visible rays have free transmission; the destruction of sounding-power by such liquids must therefore be due to the absorption of the invisible calorific rays. This induction, which hardly needs verification, is nevertheless capable thereof. Many years ago I pointed out the astonishing transparency of dissolved iodine to the invisible heat-rays. Placed in the path of the intermittent beam, a layer of this substance, perfectly opaque to light, does not sensibly diminish the sound of transparent gases and vapours. To such substances the iodine is exactly complementary, arresting the rays which they transmit, transmitting the rays which they absorb, and therefore not interfering with the sounding-power.

That sounds may also be produced by the absorption of the visible rays is well exemplified by the deportment of iodine and bromine vapours, both of which yield with the lime-light forcible sounds. Here the intervention of a transparent liquid, however adiathermanous it may be, produces no sensible effect upon the sound, the reason being that it permits the particular



rays which act upon the coloured vapours to pass freely through it. A layer of dissolved iodine, on the other hand, deprives the beam of its power of evoking sounds from either iodine or bromine vapour.

The rotation which produces the maximum effect is soon ascertained by experiment. The sound is loudest when the pulses succeed each other in periods which invoke the resonance of the flask. I possess a hollow cone with a well-polished rock-salt base, by which this point is well illustrated. Filling this cone with chloride of methyl, while the base is turned towards the source of heat, the apex of the cone being connected by a tube with the ear, sounds of extraordinary intensity are produced. Abandoning the ear-tube, the sound can be heard at a distance. But to obtain this effect the speed of rotation must be definite and constant. The maximum sound once obtained, either the lowering or the heightening of the speed rapidly enfeebles it. It is difficult by hand-turning to keep the rate of rotation constant. Hence the desirability of a mechanical arrangement which would ensure the proper rapidity and necessary uniformity. One or two motive powers have been tried, including a small steam-engine and an electro-magnetic engine; but the arrangement has not yet been brought to perfection.

### § 9. *Manometric measurements.*

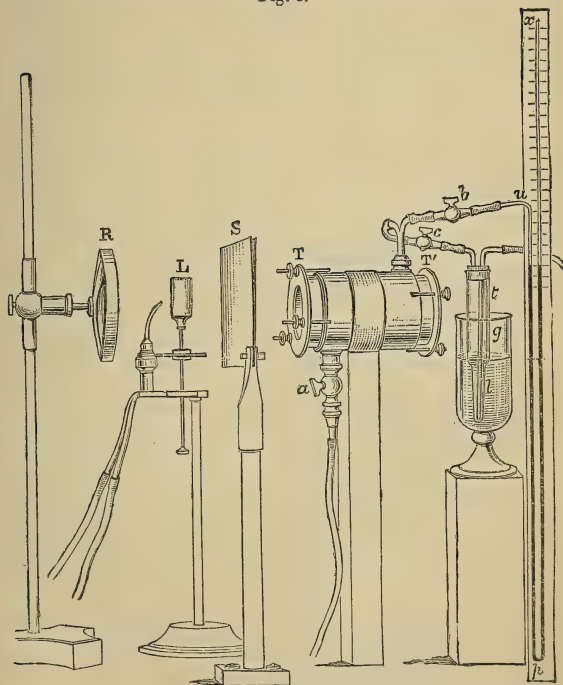
Some time before the visit of Prof. Graham Bell in November, 1880, I had inserted into my old experimental brass cylinder a narrow tube of glass, which, being bent at a right angle a few inches above the cylinder, could hold an index of coloured liquid in its horizontal portion. I had long known that the absorption of radiant heat must be accompanied by the expansion of the absorbing body, but thought that such expansion would furnish only a rough measure of the absorption. With ordinary sources of heat I found the expansion small, even when sulphuric ether occupied the experimental tube; but when a pair of stout carbons, rendered incandescent by a Siemens machine, were employed as a source, the liquid index was driven forcibly out of the narrow glass tube.

The experimental tube, however, was but a rude manometer; and I therefore sketched and described to my assistant at the time, with a view to its construction, a handier instrument. The apparatus was to consist of a short tube with rock-salt ends, capable of being exhausted and filled with any required gas or vapour. Through this tube it was proposed to send a concentrated calorific beam, whose action on an absorbent gas or vapour should be declared by the depression of a liquid column in one leg of a U tube, and its elevation in

the other. Two rock-salt plates were to be employed, with the view of allowing the beam free escape from the tube after it had done its work upon the gas or vapour. The warming of the apparatus by the reverberation of the heat would be thus avoided. The point aimed at was to effect the expansion of the gaseous body purely by radiant heat, and undisturbed as far as possible by heat derived from the envelope\*.

A number of manometric tubes of different lengths and materials were constructed on this principle, some being of glass and some of metal. The instrument with which the measurements now to be recorded were executed is represented in fig. 8. T T' is a glass tube 4 inches long and 3 inches in diameter. It is provided with brass flanges at the ends which

Fig. 8.



\* Professor Röntgen was, I believe, the first to turn the expansion of gases to account in demonstrating the absorption of radiant heat. The

reduce the diameter to 2.5 inches. Against these flanges, transparent plates of rock-salt are fixed air-tight. The tightness of the tube was secured, sometimes by india-rubber washers properly greased, and sometimes by cement\*. A stop-cock *a* near one end of T T' was connected with a barometer-tube and an air-pump. A T piece at the other end was connected on the one side with a purifying-apparatus (not shown), consisting of two U tubes, one containing fragments of Carrara marble wetted with caustic potash, the other containing fragments of glass wetted with sulphuric acid. Before entering these U tubes the air was freed from suspended matter by a plug of cotton-wool. On the other side, the T piece was connected with a quill tube of glass bent into the shape of a U, in the two legs of which a coloured liquid stood at the same level. The liquid column when standing at the same level in both arms of the U was 350 millim. high in each, while the free leg of the U rose to a height of about 500 millim. above the surface of the liquid (shortened in the figure). The source of heat was the lime-cylinder L, rendered incandescent by a flame of coal-gas and oxygen. The rays from the lime-cylinder were received by a concave mirror R silvered in front, and sent by it in a convergent beam through the manometer-tube. The focus of the beam was within the tube and near its most distant end. The gas and oxygen were supplied from gas-holders specially constructed for these and similar experiments—long experience of the futility of gas from the public mains, or compressed in iron bottles, having shown independent gas-holders which could be kept at an unalterable pressure to be essential.

The experiments were conducted thus :—A test-tube *t*, plunged in water held by the glass *g*, contained the liquid whose vapour was to be examined. Through a cork which stopped the test-tube passed a narrow tube of glass, ending in a small orifice near the bottom of the test-tube, and at a considerable depth below the surface of the liquid. To augment this depth, and to economise the liquid, the lower part of the test-tube was drawn out to half the diameter of its upper part. A second narrow tube passed also air-tight through the cork, and ended immediately beneath it. Both tubes were bent at a right angle above the cork. The manometric tube being exhausted, air freed from its carbonic acid, its moisture, and

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very day, moreover, on which I made my communication to the Society of Telegraphic Engineers, viz. the 8th of December, 1880, he forwarded to a scientific journal the announcement of his having obtained sounds from coal-gas and ammonia (see Wiedemann's *Annalen*, Jan. 1881). His subsequent experiments with aqueous vapour &c. agree with mine.

\* The absorption of the vapours by india-rubber (which was in some cases extraordinary) caused the washers to be abandoned.

its suspended matter was allowed to bubble through the liquid in the test-tube, and to pass thence into the manometric tube. To spare the oxygen in the gas-holder it was cut off during the interval between two consecutive experiments, the coal-gas being kept continually alight. When the manometric tube was filled, which was always accomplished through an orifice of fixed dimensions, the oxygen was turned on, and the cylinder was allowed to remain for one minute under the action of the intensified flame. During this time a double silver screen S intercepted the radiation. At the end of a minute this screen, which moved on an hinge, was withdrawn, the beam then passing through the mixed air and vapour. The liquid standing in the adjacent leg of the narrow U tube was immediately depressed, that in the opposite leg being equally elevated. The rise of this latter column above its starting-point, marked zero on a millimetre-scale, was accurately measured. Double this rise gave the difference of level in the two legs of the U; and this "water-pressure" expressed the augmentation of elastic force by the absorption of radiant heat.

Here follow a certain number of the measurements which have been thus made. They do not comprise the whole of the substances examined.

TABLE V.—Vapours.  
Increase of Elastic Force by Radiant Heat.

Name of Liquid.	Boiling-point.	Mean water-pressure. millim.	Character of sound.
1. Sulphuric ether . . . . .	35	300	Very strong.
2. Hydride of amyl . . . . .	30	279	"
3. Acetone . . . . .	58	267	"
4. Bromide of ethyl . . . . .	39	264	"
5. Formic ether . . . . .	55	261	"
6. Acetic ether . . . . .	74	248	"
7. Acetal . . . . .	104	237	"
8. Chloride of allyl . . . . .	46	235	"
9. Iodide of methyl . . . . .	45	233	"
10. Dichloride of ethidene . . . . .	57	217	Strong.
11. Nitrate of ethyl . . . . .	86	208	"
12. Nitrite of amyl . . . . .	99	205	"
13. Chloride of butyl . . . . .	69	185	"
14. Butyric ether . . . . .	121	183	"
15. Formic acid . . . . .	99	180	"
16. Valeral . . . . .	100	172	"
17. Valerianic ether . . . . .	144	168	"
18. Acetate of propyl . . . . .	102	166	"
19. Methylic alcohol . . . . .	—	162	"

Table V. (*continued*).

Name of Liquid.	Boiling- point.	Mean water- pressure. millim.	Character of sound.
20. Iodide of ethyl . . .	72 <sup>o</sup>	148	Moderate.
21. Bromide of butyl. . .	92	134	"
22. Dutch liquid . . .	85	127	"
23. Acetate of butyl . . .	114	120	"
24. Benzol . . . . .	81	117	"
25. Carbonic ether . . .	126	108	"
26. Chloride of amyl . . .	102	105	"
27. Chloropicrin . . . .	112	94	"
28. Iodide of allyl. . . .	101	92	"
29. Chloroform . . . . .	61	89	"
30. Iodide of butyl . . .	121	88	"
31. Allylic alcohol . . . .	97	84	"
32. Bisulphide of carbon .	43	81	"
33. Bromide of amyl. . . .	119	78	"
34. Cyanide of ethyl . . .	98	77	"
35. Butyl alcohol . . . .	110	72	Weak.
36. Nitrate of amyl . . . .	147	67	"
37. Oxalate of ethyl . . .	—	66	"
38. Cyanide of methyl . . .	82	64	"
39. Tetrachloride of carbon.	77	58	"
40. Bromoform . . . . .	150	44	"
41. Xylol . . . . .	140	44	"
42. Amylic alcohol . . . .	130	42	"
43. Iodide of amyl . . . .	146	42	"
44. Terebine . . . . .	160	39	"
45. Cymole . . . . .	175	38	"
46. Butyric acid . . . . .	163	} Very small absorptions and very feeble sounds at ordinary tempera- tures. Sounds in most cases very strong when liquid is heated to its boiling-point.	
47. Butyrate of amyl. . . .	176		
48. Caprylic alcohol . . . .	180		
49. Valerianic acid . . . .	175		
50. Pure aniline . . . . .	184		
51. Cœnanthic ether . . . .	188		
52. Valerianate of amyl. . .	196		
53. Salicylous acid . . . .	196		
54. Caproic acid . . . . .	205		
55. Nitro-benzol . . . . .	205		
56. Kreosote . . . . .	210		
57. Menthol . . . . .	213		
58. Chinoline . . . . .	238		
59. Eugenol . . . . .	247		
60. Nicotine . . . . .	250		
61. Monobromnaphthaline .	277		
62. Sebacic ether . . . . .	308		



TABLE VI.—Gases.

Name of Gas.	Water-pressure. millim.
Chloride of methyl . . . . .	350
Aldehyde . . . . .	325
Olefiant gas . . . . .	315
Sulphuric ether . . . . .	300
Nitrous oxide . . . . .	198
Marsh-gas . . . . .	164
Carbonic acid . . . . .	144
Carbonic oxide . . . . .	116
Oxygen . . . . .	5
Hydrogen . . . . .	5
Nitrogen . . . . .	5
Dry air . . . . .	5
Humid air at 50° C. . . . .	130

Sulphuric ether is here inserted with the view of connecting this Table with the last. Of all gaseous bodies hitherto examined, chloride of methyl is the most energetic absorber and the most powerful sound-producer. After it comes aldehyde, with a boiling-point of 21° C. The figure 5 attached to the elementary gases and to dry air expresses, not absorption of radiant heat, but expansion, due to contact with the slightly warmed apparatus. The nitrous oxide employed was derived from an iron bottle, in which it was preserved for medical purposes. In some of my experiments marsh-gas showed itself a better absorber than nitrous oxide. This, for instance, was the case in experiments made in the spring of 1880 with the manometer. The sample of marsh-gas wherewith the foregoing result was obtained was very carefully prepared in our chemical laboratory.

The temperature of 50° C. in the case of humid air was obtained in a wooden shed erected in our laboratory. The shed is traversed by two tubes of sheet iron 4 inches in diameter, which carry the heated air and products of combustion from two large ring burners. It is 8' 6" long, 4' 3" wide, and 7 feet high. The temperature of the air within it can be readily raised to 60° C. In the experiment recorded in Table VI. the air was taken from the outside laboratory through a tube passing through the wooden wall of the shed. It was caused to bubble through water contained in a large flask which had been permitted to remain for some time in the warm shed. The mixed air and vapour entered the manometer-tube at a temperature some degrees lower than that of the tube itself. Closely examined, all parts of this tube were bright and dry when the vapour-laden air was within it. On

permitting the beam from the lime-light (produced by coal-gas and oxygen) to pass through the mixture, a prompt rise of 65 millim. was the consequence. Cutting the beam off, the column rapidly returned to zero. The double of 65, or 130 millim., gives the difference of level in the two legs of the U tube.

I have done my best to render these determinations correct. They have been repeated both by myself and my assistant\* a great number of times. The first measurements were made in the early part of last year, and were made known in the Royal Institution on the 8th of April, 1881. Difficulties were encountered in obtaining a powerful, and at the same time constant, source of heat. The mixture of coal-gas and oxygen issuing from independent holders was finally resorted to. The sounds are classified into "very strong," "strong," &c.; but it is, of course, impossible to say where one class ends and another begins. They shade gradually into each other. But if the middle members of any class be compared with the corresponding members of another class, the difference of sounding-power will appear.

#### § 10. *Application of Results to Meteorology.*

If it be at length conceded that aqueous vapour exerts upon radiant heat the action which I so long ago ascribed to it, I think the knowledge of this action will prove of importance to the scientific meteorologist. Meteorology, as connected with heat, seems to me to abound in facts which it has hitherto been incompetent to explain. This, for example, I hold to be the case as regards the celebrated observations of Patrick Wilson of Glasgow, made a century ago. Wilson brought strongly into light the great differences which sometimes exist between the temperature of the earth's surface and of the air at a small elevation above the surface. His letter to Dr. Maskelyne on this subject is published in the Philosophical Transactions for 1780, under the title:—"An Account of a most extraordinary degree of Cold at Glasgow, together with some new Experiments and Observations on the comparative Temperature of Hoar Frost and the Air near it." On the afternoon of the 13th of January, 1780, the cold was intense, a thermometer at the high window of the observatory pointing, at 7 P.M., to 0° Fahr. At 8 P.M., Wilson and Dr. Irvine laid two thermometers upon the snow, and hung up two others in the air 2 feet above the snow. Here follow the temperatures observed on the evening of the 13th and on the morning of the 14th of January:—

\* Who has aided me in this investigation with his usual zeal and intelligence.

Time of observation.	Snow-temperature.	Air-temperature.
8½ P.M.	-12°	-0°
9 "	-14	-2
10 "	-14	-4
11 "	-17	-6
11½ "	-18	-6
½ A.M.	-20	-8
1 "	-23	-7

The sign — signifies that the temperatures were all below zero Fahrenheit. These temperatures amply justify Wilson's statement that the cold was "extraordinary." Coexistent moreover with the general cold, we have a difference of 16° between the temperature of the surface and that of the air 2 feet above it. Had the air-thermometer been hung 10 feet instead of 2 feet above the surface, the difference would have been still greater. The thermometer, moreover, must have been chilled, not only by its immersion in cold air, but also by its own radiation against the intensely cold snow. The chilling of the superficial snow was purely an effect of radiation. Beneath the surface its temperature reached +14°. Wilson filled a bread-basket with this warm snow at 2½ A.M. on the 14th. Within half an hour it had fallen 24°, and in two hours 32°.

I venture to predict that if Wilson's experiment be repeated during the cold of a Canadian winter the same result will be obtained; and it seems to me that until the action of water-vapour upon radiant heat had been discovered, no explanation of the phenomenon could have been given. It was accepted, but not accounted for. On the night of Wilson's observations "a light air was felt coming from the east." With such an "air" and such a temperature the quantity of water-vapour in the atmosphere must have been infinitesimal. Dry air being a practical vacuum to the rays of heat, were the vapour-screen entirely removed, the earth would find itself exchanging temperatures with celestial space, and the superficial chill would be commensurate. In Wilson's case, though vapour was not abolished, it was so far diminished as to produce the observed refrigeration. Meteorologists, I am informed, sometimes say that laboratory experiments, however well performed, have but little application to their field of observation\*. I,

\* Mr. Hill, the Meteorological reporter for the North-western Provinces of India, writes thus:—"There is even, on the part of some, an evident reluctance to accept the decision of laboratory experiments on the question of atmospheric absorption as final, however ingenious, varied, and consistent with one another the experiments may be" (Proc. Roy. Soc. vol. xxxiii. p. 216).

on the other hand, submit that such experiments are necessary to rescue their science from empiricism. What could Wells have done with dew had he not been preceded by Leslie and Rumford? His whole theory is an application of results obtained in the laboratory\*.

What I have stated regarding Wilson applies also to Six, who concluded from his experiments "that the greatest differences at night in point of temperature, between bodies on the surface of the earth and the atmosphere near it, are those which take place in very cold weather." This is quoted from Wells †, who, in his essay on Dew, recurs more than once to the subject. He signalizes, but does not explain, "the greater difference which takes place in very cold weather, if it be calm and clear, between the temperatures of the air and of bodies on the earth at night, than in equally calm and clear weather in summer"‡. A considerable number of observations bearing upon this point are scattered through the essay. The radiant power of the air being practically *nil*, it retains for a considerable time the warmth imparted to it during the day, while, when it is dry, the rays from the surface of the earth pass unimpeded through it. Hence the relative refrigeration of the surface§.

In regard to the action of water-vapour Magnus considered experiment superfluous, as the phenomenon of dew sufficed to prove me wrong. If the vapour possessed the power which I ascribed to it, he contended that dew could not be formed. It is not difficult to dispose of this objection. The formation of dew and superficial refrigeration are connected, not by coincidence, but by opposition. I would venture to predict that where the one is great the other, in general, will be small. "Very little dew," says Wells, "appeared on the two nights of the greatest cold I have ever observed on the surface of

\* "Its complete theory," says Wells, "could not possibly, in my opinion, have been attained, before the discoveries on heat were made, which are contained in the works of Mr. Leslie and Count Rumford" (Essays, p. 191).

† Essays, p. 176. Wells thus generously refers to the labours of Wilson:—"Indeed, several of my experiments upon dew were only imitations of some which had been previously made on hoar frost, by that ingenious and worthy man" (Essays, p. 151).

‡ Ibid. p. 188.

§ It ought to be stated that, contrary to Six and to Wells, Mr. Glaisher has found that "the differences between the temperature of the air and of bodies on the earth at night, in equally clear and calm weather, were the same at every period of the year" (Phil. Trans. 1847, p. 126). He moreover records differences considerably in excess of those observed by Wilson and by Wells. Keeping the action of aqueous vapour in view, the elaborate paper of Mr. Glaisher might repay further discussion.

the earth, relatively to the temperature of the air, both of them having occurred after a long tract of dry weather”\*. This evidence is specially valuable in view of the fact that Wells knew nothing of the action of water-vapour on radiant heat. On another occasion he observed a difference of  $9\frac{1}{2}$  degrees between the temperature of the air and that of wool placed upon the earth, without any deposition of dew whatever upon the chilled wool †. He supplements these observations by one equally important in the opposite direction. “On the night,” he writes, “which afforded the most copious dew ever observed by me, the cold possessed by the grass beyond that of the air was for the most part only  $3^{\circ}$  and  $4^{\circ}$ ” ‡. The smallness of the refrigeration in this instance, and the copiousness of the dew, I refer to one and the same cause, namely the abundance of vapour. Heavy dew implies this abundance; abundant vapour, if not too local, implies checked radiation; and checked radiation tends to abolish the difference of temperature between air and soil.

Wells had a theory of his own to account for the association of moderate refrigeration and heavy dew. The heat rendered free by the condensation of the vapour to liquid “prevented” the cold. He tried to determine the effect of condensation by the following experiment §. To 10 grains of wool he added 21 grains of water, this being the quantity of dew deposited on wool in one of his observations. He placed the moistened wool in a saucer on a feather-bed in a room, and determined the chill produced by its evaporation. After eight hours, while the wool still retained  $2\frac{1}{2}$  grains of moisture, its temperature was  $4^{\circ}$  lower than that of a dry saucer placed near it on the same feather-bed. When the process is reversed, condensation instead of evaporation coming into play, the foregoing amount of heat, Wells contended, would be liberated on the grass, and thus prevent inordinate refrigeration.

In thus reasoning Wells went to the limit of the knowledge of his time; and the explanation here given is a philosophical one. But I do not think it a sufficient explanation. The grass is exposed to the open atmosphere; and the heat deve-

\* Essays, p. 186.

† Ibid. p. 183. Wells sometimes found wetted wool to lose weight, while dry wool gained no weight though lowered many degrees below the temperature of the air (p. 184).

‡ Ibid. p. 169. From a remark occurring at page 135, it may be inferred that the night here referred to was that common to the 29th and 30th of July, 1813. On the two occasions first mentioned, when there was but little dew, the grass was in one instance  $12^{\circ}$ , and in the other  $14^{\circ}$  colder than the air.

§ Essays, p. 187.



loped by every successive film of moisture condensed upon its blades is instantly wasted by radiation. Those who are accustomed to work with the thermopile know how rapidly the associated galvanometer-needle falls from a high deflection to zero when the heat incident upon the pile is suddenly cut off. A similar rapidity of waste would assuredly occur during the slow formation of dew. The heat of condensation could not, for this reason, be housed in the manner supposed by Wells \*. The true explanation I hold to be that already indicated—the checking of radiation by vapour, the abundance of which was indicated by the copious deposition of dew.

If the experiments of Wilson could be made in an atmosphere still colder than that in which he worked—on a larger plain, for instance, and in a country remarkable for the dryness of its air—Wells considered that a difference of at least  $30^{\circ}$  would be observed on serene nights between the air and a downy substance placed on the earth. And as Six had found the air-temperature at an elevation of 220 feet to be  $10^{\circ}$  higher than at 7 feet, these  $10^{\circ}$  being added to the  $30^{\circ}$  would make the surface at least  $40^{\circ}$  colder than the air at the height of 200 or 300 feet. With all this I agree. I would go even further, and reiterate here a statement made by me nineteen years ago, that the withdrawal of the aqueous vapour of our atmosphere, for a single calm night, would kill every plant in England capable of being killed by a freezing temperature.

Pictet, I believe, was the first to notice that the temperature of the air near the earth's surface on serene nights diminished as the surface was approached, the sequence of the day temperatures being thus inverted. To account for the chilling of the air, say, at 10 feet above the earth's surface beyond that

\* Wells himself observed in grass a fall of temperature of  $7^{\circ}$  in twenty minutes. This gives us some notion of the rapidity with which a radiant so powerful as water would dispose of its heat (Essays, p. 157).

At the instance of my friend Mr. Francis Galton, and with the kind sanction of the Meteorological Council, the following instructive observations, showing the temperatures recorded by two thermometers—the one placed on cotton-wool resting on the earth, and the other hung at a height of four feet in the air—were recently made by Mr. Whipple at Kew:—

Time.	Air.	Wool.
4.20 P.M. . . . .	$34^{\circ}8$	$33^{\circ}2$
4.25   " . . . . .	$32^{\circ}5$	$27^{\circ}6$
4.30   " . . . . .	$32^{\circ}4$	$25^{\circ}7$
4.35   " . . . . .	$32^{\circ}4$	$23^{\circ}4$
4.40   " . . . . .	$32^{\circ}2$	$21^{\circ}7$
4.45   " . . . . .	$32^{\circ}2$	$20^{\circ}7$

The rapidity of radiation is well shown by these observations, an exposure of twenty-five minutes sufficing to establish a difference of  $11^{\circ}5$ .

at 100 feet above the surface, Wells invoked the radiant power of the air itself. It is chilled, he thought, by its own emission against the cold earth underneath. Wells takes great pains to prove that the air possesses this power; and if not the air, the floating matter of the air will, he contends, exert the necessary radiation. Difficulties of this nature not unfrequently crop up in works on meteorology; but they disappear in presence of the fact that mixed with the air is a gaseous constituent, small in quantity, but capable of producing the effects needing explanation.

As an example of such difficulties, I have already referred to Sir John Leslie's paper, "On certain Impressions of Cold transmitted from the Higher Atmosphere"\*. He there describes the *Æthrioscope*, an instrument used to measure these impressions. "The sensibility," he says, "of the instrument is very striking; for the liquor incessantly falls and rises in the stem with every passing cloud. Under a fine blue sky, it will sometimes indicate a cold of 50 millesimal degrees; yet on the other days, when the air seems equally bright, the effect is only 30°. The causes of these variations are not quite ascertained." He might have said, not at all ascertained. The causes, I submit, are the variations of the quantity of transparent aqueous vapour in the atmosphere, which, without affecting the visual brightness of the air, is competent to arrest radiation from the earth. Precisely of the same character is the difficulty noticed by Lieutenant Hennessey in his paper on "Actinometrical Observations in India." Like Leslie, he speaks of variations the causes of which are not ascertained. "Again," he says, "there is a change of intensity from day to day apparently not due to alterations in the sun's declination so that the average daily curve (about noon) is higher or lower without any visible reason"†. The reason here is that applicable in Leslie's case, namely the variations of the invisible atmospheric vapour.

In 1866 my friend Professor Soret, of Geneva, favoured me with a letter from which the following is an extract:—"In two comparative experiments, made within a few days at Geneva and Bologna, the most powerful radiation was obtained at Geneva, although at Bologna the heavens were visibly *purser*. The result appears to me to support your views regarding the aqueous vapour of the air; for the tension of aqueous vapour at Bologna was 10·7, while at Geneva it was only 6·33."

Cautiously abstaining from drawing a general conclusion

\* Transactions Roy. Soc. of Edinburgh, vol. viii. p. 483.

† Proc. Roy. Soc. vol. xix. p. 228.

from a single fact, M. Soret, in 1868, made some further experiments on solar radiation. The intensity was measured by first allowing the rays to fall directly on the thermometer of the actinometer, and then by allowing them, prior to meeting the thermometer, to pass through 5 centimetres of water.

Calling the first temperature  $T$  and the second  $t$ , the ratio  $\frac{t}{T}$  will be obviously greatest when the absorption by the water is least. And as we know that water exerts its chief absorbent power on the ultra-red rays of the spectrum, the variations in this ratio observed at different atmospheric thicknesses will enable us to infer the nature of the heat "arrested" by the atmosphere.

M. Soret found the ratio to be greater in the middle of the day than when the sun is near the horizon. At 12.30, for example, on the 9th of March the ratio was 0.594, while at 5.10, on the same day, it was only 0.409. A smaller fraction of the total heat was absorbed by the water near midday than near sunset. At midday, therefore, the solar heat was more thoroughly sifted of its calorific rays, and more transmissible by water, than it was when the atmospheric thickness was much greater. It would seem difficult to reconcile this result with the notion that aqueous vapour is the absorbing constituent of the atmosphere.

A year subsequently MM. Desains and Branley found, both at Paris and at Lucerne, that the sun's heat was always more transmissible through water and alum in the morning than at midday. I have too much confidence in the able experimenters here named to think any of them wrong. How, then, is the discrepancy between them to be accounted for? I think in the following way. What is called the glow of the Alps varies greatly with the quantity of suspended matter in the air. When pronounced, it shows that the more refrangible constituents have been in great part removed from the sun's rays. The proportion of the less-refrangible rays in the total radiation is augmented in this way, the relative transmissibility of the heat being diminished. It was, I would suggest, heat that had its character impressed upon it in this way by scattering, and not by absorption, that yielded the result obtained by M. Soret.

Whatever may be the value of this explanation, one result of great interest to me was established by the two French experimenters. Simultaneous observations were made by them on the summit of the Rigi and at Lucerne, the vertical distance between both stations being 4756 feet. Within this stratum 17.1 per cent. of the solar rays was absorbed.

Experiments were made at the same time at both stations on the perviousness of water to the solar rays. If, as I contend, a vapour and its liquid absorb the same rays, the withdrawal of 17 per cent. of the radiation by aqueous vapour must render the residual heat more transmissible by water. This is precisely what the French experimenters found it to be. "Through a glass trough 0·08 of a metre in length, and full of water, the rays on the Rigi passed in the proportion of 685, and at Lucerne in the proportion of 730, per 1000 of the incident heat."

Magnus was so convinced of the impotency of aqueous vapour to arrest radiant heat, that in reference to various meteorological phenomena, where the action I had ascribed to it offered a satisfactory explanation of the facts, he put in its place mist or haze, the existence of which he assumed, even when neither mist nor haze was visible. There are various passages in the Essay on Dew which it would be difficult to reconcile with this assumption; for they show that even visible atmospheric turbidity has by no means the influence which Magnus ascribed to it.

Thus, on the 7th of January, 1814, Wells observed, "a little after sunset," a refrigeration of  $8^{\circ}$ , at a time when some parts of the sky were covered with clouds, and the lower atmosphere a little obscure\*. On another evening, "when the atmosphere was neither very clear nor very still," a difference of  $14\frac{1}{2}^{\circ}$  was observed between the temperatures of air and swan-down. Wells also observed a refrigeration of  $5^{\circ}$  when the sky was thickly covered with high clouds. A very definite observation in regard to haze was made on the 21st of January, 1814. The air at this time was "a good deal hazy"†. Notwithstanding this, the temperature of swan-down placed on snow was  $13\frac{1}{2}^{\circ}$  lower than that of the air 4 feet above it. Thus, if other circumstances be favourable—that is to say, if the air be dry—even a visible haze does not prevent powerful refrigeration. I close these references to mist and haze by mentioning a most striking observation made by Wells on the 1st of January, 1814. "I found," he says, "during a dense fog, while the weather was very calm, a thermometer lying on grass thickly covered with hoar frost  $9^{\circ}$  lower than another suspended in the air 4 feet above the former"‡. Here, as before, low temperature implies scanty vapour, the absence of which enabled the grass to pour its heat even through the interstices of a dense fog§.

\* Essays, p. 174.

† Ibid. p. 176.

‡ Ibid. p. 158.

§ Mr. Glaisher moreover has found differences of from  $10^{\circ}$  to  $12^{\circ}$  between grass and air "at times when the sky has been free from clouds but not bright, haze and vapour being prevalent" (Phil. Trans. 1847, p. 145).

I could draw still further on this admirable Essay in illustration of the thesis which I have so long defended. As a repertory of valuable facts and penetrative arguments it probably stands unrivalled in the literature of meteorology. One point remains which cannot be passed over. It has reference to the part played by clouds in arresting and returning the radiation from the earth. "No direct experiments," says Wells, "can be made to ascertain the manner in which clouds prevent, or occasion to be small, the appearance of a cold at night, upon the surface of the earth, greater than that of the atmosphere; but it may, I think, be firmly [fairly?] concluded from what has been said in the preceding article, that they produce this effect, almost entirely, by radiating heat to the earth, in return for that which they intercept in its progress from the earth towards the heavens"\*. Wells had the strongest analogies to adduce in favour of this view. He placed boards and sheets of paper above his thermometer, thus screening them from the clear sky; and in that beautiful passage where he speaks of "the pride of self-knowledge," and refers to the simple devices which experience had taught gardeners to apply for the safety of their plants, he mentions the protection which even a thin cambric handkerchief can afford to thermometers over which it is spread. He was irresistibly led to conclude that clouds acted in the same fashion, and that when they occupied the firmament, they sent back to the earth the heat incident upon them, exactly as the board, and the paper, and the cambric sent it back in experiments made close to the surface of the earth.

But in the enunciation of this hypothesis his knowledge and penetration as an observer came, as usual, into play. He is careful to distinguish between high clouds and low clouds. "Dense clouds," he says, "near the earth must possess the heat of the lower atmosphere, and will therefore send to the earth as much, or nearly as much, heat as they receive from it by radiation. But similarly dense clouds, if very high, though they equally intercept the communication of the earth with the sky, yet being from this elevated situation colder than the earth, will radiate to it less heat than they receive from it, and may consequently admit of bodies on its surface becoming several degrees colder than the air"†.

Magnus urged this point against me; and I may be per-

\* Essays, p. 205.

† Ibid. p. 206. "If," says Wells, in another place, "the clouds were high and the weather calm, I have sometimes seen on grass, though the sky was entirely hidden, no very inconsiderable quantity of dew" (ibid. p. 128),



mitted to say that I always considered it one of his strongest points—my holding of this opinion being, however, dependent on the views which I entertained, and which were opposed to those of Magnus, regarding the relation of liquid to vapour. If, as I believe, the absorbent power is not enhanced by condensation—if in this respect water behaves like hydride of amyl and sulphuric ether,—then I do not think that such a process of reverberation, between earth and clouds, as that assumed by Wells is possible. The aqueous vapour, in a very few thousand feet of air, of average humidity, would, if condensed, form a layer of water 0·5 of an inch in thickness; and through such a layer, or even through a thinner layer, the earth's radiation could not pass. If the earth's radiation reach the clouds, it must be by a process similar to that of handing buckets from man to man in the case of a fire. The heat must be taken up and re-radiated, we know not how many times, before the clouds are reached. I do not, however, think this mechanism of discharge necessary. Low clouds will not form above exposed thermometers, in weather previously serene, unless some change has occurred in the atmosphere; and change may occur where no cloud reveals it. It may extend, and in most cases probably does extend, from the low clouds to the earth. I think it in the highest degree probable that in most, if not in all, the cases cited by Wells of thermometers rising when clouds were formed overhead, the precipitation was due to the intrusion of humid air, the humidity extending invisibly from the clouds downwards. To this, I believe, rather than to any immediate exchange of temperature with the clouds, the rapid and considerable changes of temperature referred to by him at pp. 156 and 157 of the Essay are to be ascribed. Future observations will, doubtless, bring this view to an experimental test.

I here recur with renewed pleasure to a paper published by General Strachey in the Philosophical Magazine for July 1866. It was probably intended as a reply to the strictures of Magnus; and to me it appears cogent in the highest degree. General Strachey calculated the fall of temperature from 6<sup>h</sup> 40<sup>m</sup> P.M., Madras time, to 5<sup>h</sup> 40<sup>m</sup> next morning, for a certain number of days, selected as sufficiently clear. He also calculated the mean vapour-tension during the nights, and tabulated the results according to the quantity of vapour, for the years 1841, 1842, 1843, and 1844. In such observations, as pointed out by Strachey, discrepancies are to be expected; but the general result is unmistakable, that the fall of temperature by radiation is greatest when the air is driest, and least when the air is most humid. A series of observations

made at Madras between the 4th and the 25th of March, 1850, are particularly suitable for the illustration of this law of action. During the period referred to "the sky remained remarkably clear, while great variations of the quantity of vapour took place." Here are the results as tabulated by General Strachey:—

Tension of vapour.	·888.	·849.	·805.	·749.	·708.
Fall of temperature from 6 <sup>h</sup> 40 <sup>m</sup> P.M. to 5 <sup>h</sup> 40 <sup>m</sup> A.M. }	6°·0	7°·1	8°·3	8°·5	10°·3
Tension of vapour.	·659.	·605.	·554.	·435.	
Fall of temperature from 6 <sup>h</sup> 40 <sup>m</sup> P.M. to 5 <sup>h</sup> 40 <sup>m</sup> A.M. }	12°·6	12°·1	13°·1	16°·5.	

These results, if correct (and I am not aware that they have ever been questioned), show in the most impressive manner the influence of the aqueous vapour of our atmosphere on our planet's radiation. As the vapour diminishes, the door opens, which permits the escape of the earth's heat. The halving of the vapour-tension nearly trebles the refrigeration of the thermometer.

Equally clear is the evidence given by General Strachey as to the action of aqueous vapour upon the radiation of the sun. Here are the results:—

Tension of vapour.	·824.	·737.	·670.	·576.	·511.	·394.
Rise of temperature from 5 <sup>h</sup> 40 <sup>m</sup> A.M. to 1 <sup>h</sup> 40 <sup>m</sup> P.M. }	12°·4	15°·1	19°·3	22°·2	24°·3	27°·0

This table is the exact complement of the last. *There* the *fall* of temperature was powerfully promoted by the withdrawal of the vapour. *Here* the *rise* of temperature is powerfully promoted by the same cause\*.

\* Mr. Hill, Meteorological Reporter for the North-west Provinces of India, in a paper recently presented to the Royal Society, describes an attempt to determine the "Constituent of the Atmosphere which absorbs Radiant Heat." He uses for this purpose the careful observations made by Messrs. J. B. N. Hennessey and W. H. Cole, at Mussoree and Dehra respectively. From the absence of symmetry in the quantities of heat received by the actinometer on both sides of noon at Mussoree, and from the existence of this symmetry at Dehra, he infers the periodic lifting and lowering of the absorbing constituent above and below the higher station. He finds the variation of the absorption-coefficient to follow the variations

But the most impressive illustration of the action of aqueous vapour is now to be referred to. In 1865 I subjected to examination the radiation from the electric light produced by a battery of 50 of Grove's cells, and found, by prismatic analysis, the invisible calorific radiation to be 7.7 times the visible. The determination was afterwards made by the method of filtration, whereby the one class of rays was detached with great sharpness from the other, and both of them rendered measurable. By this method the invisible radiation was found to be 8 times the visible. A close agreement was therefore established between the results of the two methods. Computed from the diagram of Müller, the invisible radiation of the sun is twice the visible. This smaller ratio might, of course, be referred to the original quality of the solar emission, the ratio holding good up to the surface of the sun. But having placed, as I thought beyond doubt, the action of aqueous vapour on radiant heat, and believing the action of the vapour to be substantially the same as that of water, I reasoned and experimented as follows in 1865:—"The sun's rays, before reaching our earth, have to pass through the atmosphere, where they encounter the atmospheric vapour, which exercises a powerful absorption on the invisible calorific rays. From this, apart from other considerations, it would follow that the ratio of the invisible to the visible radiation in the case of the sun must be less than in the case of the electric light. Experiment, we see, justifies this conclusion. If we cause the beam from the electric lamp to pass through a layer of water of suitable thickness, we place its radiation in approximately the same condition as that of the sun; and on decomposing the beam after it has been thus sifted, we obtain a distribution of heat closely resembling that observed in the solar spectrum."

If, therefore, we could get above the vapour-screen which swathes the earth, the "powerful absorption" referred to in the paragraph just quoted would disappear, the ratio of the invisible to the visible solar rays being augmented correspondingly. That such would be the case I have long taken for granted; but I hardly hoped for a corroboration so impressive as that furnished by the recent observations of Pro-

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of vapour-tension. From this and from a similar result obtained by a second method of calculation, he draws the conclusion "that there can be very little error in agreeing with Dr. Tyndall that the absorptive power of dry air is sensibly nothing, and that the total absorptive power of the atmosphere is due to the water-vapour it contains." A most interesting discourse on Solar Heat, by M. Violle, of Grenoble, will be found in the *Revue Scientifique* for 1878, p. 944. I guard myself against saying that the diathermancy of dry air is *perfect*.

fessor Langley, in the Sierra Nevada Mountains of California. Professor Langley is known to have highly distinguished himself by researches on radiant heat, with instruments of his own invention. He writes to me thus from Mount Whitney, California, September 10, 1881:—

“I received your letter just as I was starting on the expedition to this point of which I wrote. I much regretted that I had not time to provide myself with your mercury-pyrheliometer; so I have been obliged to use the old form, with its many disadvantages.

“Our route here has led us through the dryest parts of this continent, and across rainless deserts to this mountain, where the air is perhaps drier than at any other equal altitude ever used for scientific investigation. I write from an altitude of 12,000 feet, while the ‘Peak’ rises nearly 3000 more above me. I have been successful in bringing up, and using here, the rather complex and delicate apparatus for investigating the absorption of the atmosphere on homogeneous rays, throughout the visible and invisible spectrum.

“You may be interested in knowing that the result indicates a great difference in the *distribution* of the solar energy here from that to which we are accustomed in regions of ordinary humidity; and that while the evidence of the effect of water-vapour on the more refrangible rays is feeble, there is, on the other hand, a systematic effect due to its absence, which shows by contrast its power on the red and ultra-red in a striking light.

“These experiments also indicate an enormous extension of the ultra-red spectrum beyond the point to which it has been followed below, and, being made on a scale different from that of the laboratory—on one indeed as grand as nature can furnish—and by means wholly independent of those usually applied to the research, must, I think, when published, put an end to every doubt as to the accuracy of the statements so long since made by you, as to the absorbent power of this agent over the greater part of the spectrum, and as to its predominant importance in modifying to us the solar energy.

“I am, with much regard,

“Very truly yours,

“S. P. LANGLEY.”

LXIV. *On Rhabdophane, a new Mineral.*By W. G. LETTSOM, *Esq.*\*

HAVING ascertained from Monsieur Lecoq de Boisbauran, who had had the kindness to favour me with a specimen of his new metal gallium, that it would be agreeable to him to examine our British blendes for that metal, I applied to various dealers for specimens thereof, and I also asked a few friends to give me their assistance in the matter. Among the latter was Mr. Ludlam, who with his usual liberality sent me three or four specimens.

Among them was one which in its appearance differed from any British blende that I am familiar with. It was in small mamillated globules, brown, with a peculiar greasy lustre. Having a suspicion that possibly it might not be a blende, I submitted it for examination to that Grand Inquisitor the spectroscope.

Letting a bright light fall on the specimen, I looked at it with a pocket-spectroscope, when immediately the bands due to the presence of didymium became apparent. I had thus come across what, at least, was no ordinary blende.

Having submitted the specimen to Mr. Maskelyne, that gentleman was so good as to cause a preliminary chemical examination of the mineral to be made, from which it appears that it contains neither zinc nor sulphur, and is consequently no blende, but that it is *essentially* a phosphate of didymium.

With some pure fragments of the mineral which I have placed in the skilful hands of Mr. Walter Noel Hartley, that gentleman has kindly undertaken to make a complete analysis†

\* Communicated by the Crystallological Society, having been read November 23, 1878.

[This paper was withheld from publication with the intention that it and the analysis should appear simultaneously. Through some misapprehension this intention has not been carried out, and the analysis has already appeared in the Journal of the Chemical Society for May.—SEC. CRYST. SOC.]

† [Professor Hartley's analysis shows it to be a hydrated phosphate of cerium, didymium, and yttrium, capable of representation by the formula  $R_2O_3 \cdot P_2O_5 \cdot 2H_2O$ , the percentage composition found being :—

Combined water	.....	7.97
$P_2O_5$	.....	26.26
$Ce_2O_3, Di_2O_3, Yt_2O_3$	..	65.75

$Ce_2O_3 : Di_2O_3 : Yt_2O_3 = 23.19 : 34.77 : 2.39$  nearly.

This seems to be the first time that yttrium has been found in a British mineral.]



of the substance ; but as he informs me he has no leisure to go into the matter at present, I am not as yet able to state to the Society what is the precise constitution of the mineral.

Within a few days after showing the original specimen to Mr. Maskelyne, I had the pleasure of learning from him that he had been enabled, I believe by means of the spectroscope, to recognize two other specimens of the mineral in the old collection at Oxford, where they are simply labelled "Blende from Cornwall" \*.

On my showing Mr. Ludlam the specimen I had received from him, he informed me that it came from "the Turner Collection," which is now in his possession—and that it is described in the third volume of M. Lévy's Catalogue of that Collection, under the heading of "*Zinc sulfuré No. 75. Mamelonné, brun, fibreux dans la cassure, ressemblant au plomb-gomme, avec plomb phosphaté, Cornouailles.*" I should not say the specimen resembles plomb-gomme much ; neither have I observed any phosphate of lead upon it.

There were two specimens of the mineral in the Turner Collection as well as in the collection at Oxford, the locality attributed to them all being simply "Cornwall;" and as M. Lévy's Catalogue was published in 1837 (that is to say, more than forty years ago), I fear there is but little hope of ascertaining at what mine they were raised: even, however, if that were made out, it seems improbable the workings there should be still carried on.

Neither in the collection at the British Museum, free access to which has been kindly granted to me, nor in that at King's College, nor in the old collection belonging to Mr. Vicary at Exeter, nor in that of the late Sir John Aubyn at Devonport have I been able to find a specimen of the mineral in question.

The name *Rhabdophane*, which this species has received, was selected as one indicating the stripes or bands which it exhibits in the spectroscope.

For the information of such of our chemists as may feel disposed to work upon British blendes for gallium, I here subjoin the results that were obtained by M. Lecoq de Boisbaudran in operating upon some of those specimens that I forwarded to him. The quantity of material used for the examination was, I believe, in every case 20 grammes.

No. 1. Redruth . . Poor enough.

No. 2. Cumberland. . Rich enough.

\* There is a small specimen without label in the Brooke Collection at Cambridge.

- No. 3. Derbyshire . . No gallium.  
No. 4. Cornwall (?) . Rich enough.  
No. 5. Weardale . . Rich in gallium. Seems to be a  
little richer than the preceding.  
No. 6. Fowey Consols. Rich. Seems to be somewhat  
richer still than the preceding.

M. Lecoq de Boisbaudran adds that some of the English blends thus appear to him to be at least as rich in gallium as the Bensberg blende is, and that, judging from the intensity of the gallium-lines shown, he is inclined to think the Fowey-Consols blende is even superior to that from Bensberg.

I should add that the Fowey-Consols blende here spoken of is the well-known mamillated nodular material of that locality.

Should any member of the Society wish to see a portion of the original specimen, or to examine with the spectroscope sections thereof or of the Oxford mineral, I am prepared to submit them to him.

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LXV. *On the Dichroism of two European Andalusites.*

*By W. G. LETTSOM, Esq.\**

**T**WO years ago or so there was received in London from Brazil a batch of Andalusites, the transparency of which allowed of their remarkable dichroism being well observed. This induced me to make trial as to the amount of dichroism which Andalusites from European localities might exhibit if suitably cut by a lapidary; for none of our Andalusites that I am acquainted with are capable of being examined, as is the case with Brazilian specimens, in their natural state.

I beg leave to lay before the Society a few sections of Andalusite from a locality in Germany the name of which I have not at hand, but which I hope to obtain in a day or two. Those sections show in one image a rich chocolate-brown colour, the other being all but colourless.

Other sections, from Goldenstein in Moravia, exhibit, in one image a deep blood-red colour, the other image in this case too being almost colourless.

\* Communicated by the Crystallogical Society, having been read November 23, 1878.

LXVI. *On the Dimensions of a Magnetic Pole in the Electrostatic System of Units.* By C. K. WEAD\*.

IN the May number of this Magazine, p. 376, Dr. Everett presents Clausius's deduction of the dimensions of a magnetic pole in the electrostatic system, finding them to be  $P_e = M^{\frac{1}{2}} L^{\frac{1}{2}} T^{-2}$ , instead of  $M^{\frac{1}{2}} L^{\frac{3}{2}}$ , as Maxwell gave it without explicit statement of the method of derivation. In Maxwell's treatise this unit is obtained, along with all the rest, from fifteen simultaneous equations involving twelve unknown quantities; the substitution of the final results in the original equations shows that the suggestion of a misprint may be set aside at once.

In the smaller books that use the clearer method of deriving the dimensions step by step, the development does not usually include magnetic quantities under the electrostatic system: they are not found in the British-Association Reports on Electrical Standards, Reprint, p. 80, nor in Kohlrausch's 'Physical Measurements,' nor in Everett's 'Units and Physical Constants.' Only in Herwig's *Physikalische Begriffe*, p. 78, do I find any values for intensity of a magnetic field, moment of a magnet (strength of pole is involved in this, but not given separately), and magnetic potential in this system. An examination of his method, which leads to Maxwell's results, shows at once that the whole question turns on the step, or steps, between current-strength and magnetic moment. Using so far as possible Everett's notation, but with the subscript letter *e* or *m* to distinguish the two systems when necessary, we shall have to consider Strength of current *C*, Intensity of a magnetic field *I*, Moment of a magnet  $\mu$  or  $PL$ , Strength of magnetic pole *P*, Quantity of electricity *Q*.

Herwig gives  $I^e = \frac{2\pi r^2 C^e}{L^3}$ ; and since  $C_e = M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-2}$  (agreeing with Everett),  $I_e = \frac{C_e}{L} = M^{\frac{1}{2}} L^{\frac{1}{2}} T^{-2}$ .

Then, since a magnet whose moment  $\mu$  in the field *I* is subject to a couple,  $I_e \mu_e =$  a couple,

$$\mu_e, \text{ or } P_e L = \frac{M L^2 T^{-2}}{M^{\frac{1}{2}} L^{\frac{1}{2}} T^{-2}} = M^{\frac{1}{2}} L^{\frac{3}{2}};$$

$$P_e = M^{\frac{1}{2}} L^{\frac{1}{2}};$$

$$V_e = \frac{\text{work}}{P_e} = \frac{M L^{\frac{1}{2}} T^{-2}}{M^{\frac{1}{2}} L^{\frac{1}{2}}} = M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-1} = \text{magnetic potential.}$$

\* Communicated by the Author.

Clausius gives " $C \times L^2 = P \times L$  in any consistent system ;" so

$$P_e = \frac{C_e L^2}{L} = \frac{L^2 \times M^{\frac{1}{2}} L^{\frac{1}{2}} T^{-2}}{L} = M^{\frac{1}{2}} L^{\frac{5}{2}} T^{-2}.$$

The equation  $C \times L^2 = P \times L$  leads to  $\frac{P}{L^2} = \frac{C}{L}$ ; which would in the electromagnetic system be consistent, since each member = I. Again,  $PL = \mu$ ; that is,  $PL$  must represent a magnet; consequently  $C \times L^2$  is put equal to a magnet. But the passage of the current ordinarily produces effects, such as the movement of a galvanometer-needle, which we explain more naturally by saying that the circular current produces a magnetic field at its centre, than by saying that the current is, or makes, or even is equivalent to, a magnet. Herwig's derivation, therefore, in which a magnet placed in a field experiences a couple, conforms to the ordinary way of thinking better than the way of Clausius, and is the way used in the derivation of the electromagnetic system. Again, if

$$P_e = M^{\frac{1}{2}} L^{\frac{5}{2}} T^{-2},$$

then

$$I_e P_e L = M^{\frac{1}{2}} L^{\frac{1}{2}} T^{-2} \cdot M^{\frac{1}{2}} L^{\frac{5}{2}} T^{-2} \cdot L = M L^4 T^{-4} = \text{a couple} \times L^2 T^{-2}.$$

How can this result be explained, consistently with the known effect of a circular current on a magnet? It may be noted that, in all discussions except that of Clausius, the magnet pole  $P$  is introduced into a field. Clausius produces a field by the pole  $P$ . Also that the ratio of the two values of  $P$  is the square of a velocity.

Herwig says, with regard to the step from  $I$  to  $\mu$  in the electrostatic system:—"It may be remarked that for this purpose we cannot use the formula of § 64,  $\mu = \pi r^2 C$ , which expresses the relation between the magnetic moment  $\mu$  and the current-strength  $C$ ; for the validity of this formula is dependent (*geknüpft*) on the use of the magnetic system" (p. 78).

A comparison of the derivation of the same units in the two systems will strengthen our belief in the view, that Clausius has proposed a new way, for which, rather than for the older one, a justification is needed. Taking the least number of steps that will lead from  $P$  to  $Q$ , or *vice versâ*, we have these equations in each system:—

Magnetic,

$$\frac{PP}{L^2} = F (= \text{a force}). \quad PL = \mu; \quad I\mu = \text{a couple}; \quad \frac{CL}{L^2} = I;$$

$$Q = CT. \quad . \quad . \quad (1)$$

Electrostatic,

$$\frac{QQ}{L^2} = F. \quad \frac{Q}{T} = C; \quad \frac{CL}{L^2} = I; \quad I\mu = \text{a couple}; \quad \mu = PL. \quad (2)$$

Electrostatic (Clausius),

$$\frac{QQ}{L^2} = F. \quad \frac{Q}{T} = C; \quad CL^2 = \mu = PL. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

It is obvious at a glance that, after the fundamental operation has been performed of finding  $P_m$  or  $Q_e$ , the remaining operations take exactly the opposite order in the two systems; the corresponding equations in the two are the same; while this is not true of series (1) and (3). In (1) we may find the dimensions of  $Q$  in terms of  $P$ , and from (2) and (3) of  $P$  in terms of  $Q$ . The results are:—

$$Q_m = ML^2 T^{-1} \div P_m, \quad . \quad . \quad . \quad . \quad . \quad (1')$$

$$P_e = ML^2 T^{-1} \div Q_e, \quad . \quad . \quad . \quad . \quad . \quad (2')$$

$$P_e = LT^{-1} \div Q_e. \quad . \quad . \quad . \quad . \quad . \quad (3')$$

Since in the two systems  $P$  and  $Q$  play similar parts, are we not justified in expecting such a symmetry as is shown by (1') and (2'), rather than the want of it shown in (1') and (3')? If the values of  $P_m$  and  $Q_e$ ,  $M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-1}$  are substituted in the above, we may group the results thus:—

$$P_m = M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-1}, \quad Q_e = M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-1};$$

$$Q_m = M^{\frac{1}{2}} L^{\frac{3}{2}}, \quad P_e = M^{\frac{1}{2}} L^{\frac{3}{2}} (2'), \text{ or } M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-2} (3').$$

Of course these are not presented as three independent lines of argument in favour of Maxwell's view, as they are all involved in the series of operations (1), (2), and (3).

It will now be shown that to write " $C \times L^2 = PL$  in any consistent system" is simply begging the whole question.

No physical formulæ are better established than those used in finding with the magnetometer  $M$  and  $H$ , the moment of a magnet and the horizontal component of the earth's magnetism:—

$$MH = \frac{\pi K}{t^2(1+\theta)}; \quad \frac{M}{H} = \frac{1}{2} \frac{\gamma^5 \tan \phi - \gamma'^5 \tan \phi'}{\gamma^2 - \gamma'^2};$$

in which  $K$  = a moment of inertia =  $ML^2$ ,  $t$  = a time =  $T$ ,  $\gamma$  and  $\gamma'$  are lengths =  $L$ , and the other quantities in the second members are numerical. In the usual notation, therefore,  $\mu I = ML^2 T^{-2}$ ,  $\mu \div I = L^3$ ; whence we find the dimensions of  $\mu = M^{\frac{1}{2}} L^{\frac{3}{2}} T^{-1}$ , and of  $I = M^{\frac{1}{2}} L^{-\frac{1}{2}} T^{-1}$ , the same as in the magnetic system. But one has the same right to declare that "in any consistent system" both the above formulæ must be



true as that  $C \times L^2 = P \times L$ . In the magnetic system both are true; in the electrostatic system with Maxwell's value the first is true, the second is not; with Clausius's values the second, and not the first. Maxwell (or at least Herwig) openly uses the first; Clausius impliedly uses the second; for if  $CL^2 = PL = \mu$ , and  $C \div L = I$ ,

$$(C \div L) \times L^3 = \mu, \therefore \mu \div I = L^3.$$

In deducing the dimensions of physical quantities, there is much that is as arbitrary as the order in which several numbers shall be multiplied together\*. Thus, the familiar equation

$$I = k \frac{2\pi r^2 C}{(l^2 + d^2)^{\frac{3}{2}}}$$

where  $r$  is the radius of the current-circle, and  $d$  the distance from the centre on a normal to the plane. In the electrostatic and electromagnetic systems, the dimensions of either  $C$  or  $I$  being given to find the other,  $r$ ,  $l$ , and  $d$  being lengths,  $k$  is arbitrarily made equal to 1, and then  $I$  or  $C$  is found: if  $I$  and  $C$  had both been given, ordinarily its value would not be 1, nor its dimensions  $= L^0 M^0 T^0$ . To pass from  $I$  to  $P$  or to  $PL = \mu$ , either of two equations may be used:—

$$I = kP \div l^2; \dots \dots \dots (1)$$

$$\mu I = k' \times \text{a couple.} \dots \dots \dots (2)$$

Clausius arbitrarily makes  $k=1$  in (1), letting  $k'$  assume whatever concrete value will satisfy (2). Herwig, to obtain Maxwell's result, as arbitrarily makes  $k'=1$ , paying no attention to  $k$ . If arbitrarily we make  $k=k'=1$ ,  $\mu$  and  $I$  must come out as in the magnetic system.

In making  $k'=1$  rather than  $k$ , there is the advantage of introducing a mechanical unit; and we use the equation (2) that is both more familiar in experimental work, and the one used in the derivation of the magnetic system. Further, if  $P$  be changed, three other quantities of the twelve that Maxwell discusses must have their dimensions changed, and confusion would be introduced into his system, that is based on fifteen equations, in each of which the second member is some simple mechanical quantity, as work, time, &c. Until it has been clearly shown how this system will be affected by the proposed change, and why the new expression is to be preferred to the older one, that has been "unimpeached" for some twenty years, is it not clearly better to write  $P_e = M^{\frac{1}{2}} L^{\frac{1}{2}}$ ? It is not a question merely of correctness, but of consistency, simplicity, and usefulness; and on all these grounds Maxwell's expression seems to the writer to deserve the preference.

University of Michigan,  
Ann Arbor, May 29, 1882.

\* On this point, compare Everett's 'Deschanel,' p. 783.

LXVII. *Notices respecting New Books.*

*Magnetism and Electricity; an elementary Text-book for Students.*  
By RICHARD WORMELL, D.Sc., M.A. London: Thomas Murby.

THIS book is one of a series—the High School Science series. The author informs us that he has aimed at embodying two characteristic features—*first*, to make the work progressive in several respects from beginning to end, and, *secondly*, to introduce the explanation of the latest discoveries and applications of electricity. The latter feature will be commended by every one, but the former will appear to many to be of doubtful utility. Probably it is on that account that the book is thrown into the form of lectures. But are not the functions of a text-book and of lectures different?

A text-book ought to be clear in statement, exact in information, and free from error. We cannot say that these conditions are completely satisfied by Dr. Wormell's book. As regards the first point, there is frequently an ambiguous use of the pronoun *it*, which is not only inelegant, but causes the reader some pains to find out what is meant. For example, "But after the pith-ball has been in contact with the glass rod, it no longer comes towards it, but flies away" (p. 75). "If we rub the glass with silk, then balance it and present the finger to it, it is attracted" (p. 78). "On presenting the knuckle to the cover A, after it is lifted off, a spark of positive electricity passes to it, and the plate is discharged" (p. 88). "If a bar magnet is brought near this loop, it will be made to turn, following the bar magnet, or being repelled from it" (p. 31). The *Carrier* is described as follows:—"This consists of a metallic ball, a wooden ball covered with tin-foil, a gold-leaf, or some similarly conducting material, attached either to a glass handle or suspended by a silk thread, in order to insulate it." A tyro in electricity is not likely to discern the meaning of this description at first sight.

Owing, probably, to the progressive character of the book, many of the statements are not exact enough. Is there any advantage in making a science simpler than it really is? For example, it is said of the *Carrier* (*loc. cit.*):—"The charge of electricity brought by the carrier is of the same kind as that of the body to be tested, and affects the electroscope exactly in the same way as if the body itself were brought near it." At pp. 52 and 71 magnets and magnetic poles are mixed up in a manner which will give the student some trouble to unravel. What is meant by "placing two magnets at unit distance apart"? We have the analogy between *potential* and *level* carried a little further than usual, thus:—"The electrical capacity of any body may be measured by the quantity of electricity required to charge it to a given potential; just as the capacity of a cistern for water may be measured by the quantity of water required to fill it to a given level" (p. 111).

As regards the third point, we have at p. 51 a contradiction within the compass of a paragraph. "If we could increase the weight of the bob without altering the amount of substance composing it, we should lessen the number of oscillations per minute;"

and "If we wish to double the number of oscillations per minute we must multiply the force by four, etc."

As regards the woodcuts, we notice one very commendable feature—namely the introduction of a symbolical figure to represent a battery, electrometer, or other instrument frequently occurring in experimental arrangements. In the description of Winter's electrical machine, reference is made more than once to a knob P; but in the woodcut no P is discernible.

*The Calendar of the Departments of Law, Science, and Literature of the Tokio Dai-Gaku (University of Tokio), 1880–81.*

THE scientific papers of the Tokio University have been previously noticed (Phil. Mag. vol. xiii. p. 367, May 1882); and the above work will show the interest and importance which the Japanese government attach to the progress of education by the establishment of the Tokio Dai-Gaku or University, which could not have attained to its present state of progress had it not been favoured by the generosity of the Government, in devoting a large amount of money for instruction in the higher branches of study; and it is the intention of the authorities connected with it, while pursuing its original object, to still further make such possible improvements that the standard of scholarship attained in it may equal that of the Universities of Western countries.

The historical summary contains a brief sketch of the rise and progress of education from the introduction of Western learning in the early part of the last century, when medical science and astronomy became gradually known to the people; and subsequently to 1744 three observatories were established, two at Asakusa and one on the hill at Kudan, in which astronomical observations were made, and an almanac was compiled.

In the beginning of the present century, about 1811, it was considered a pressing necessity to understand the condition of foreign nations, and to adopt such of the better arts as they might have. Accordingly Dutch works were first translated and the Dutch language taught, to which, in 1857, English, French, German, and Russian were added, and courses of Mathematics, Chemistry, and Botany successively established.

After this time, in 1862, various modifications and improvements in the educational department took place; instruction in German, French, and English was given; but in 1875 all this was altered, and the latter language was only to be used. Students, however, were sent to other countries to continue their studies.

Since the first permanent establishment of the Tokio Dai-Gaku various modifications have been made, until it has arrived at its present state, which embraces the departments of the Law, Science, Literature, and Medicine.

Although the special courses of instruction are mainly given in the English language, and the student is taught either French or German, it is the intention ultimately to use the Japanese language in all the Departments.

LXVIII. *Intelligence and Miscellaneous Articles.*

ON THE EFFECTS PRODUCED IN A VACUUM BY THE CURRENT OF  
THE GRAMME MACHINES. BY M. JAMIN.

AS soon as Davy had discovered the electric arc he hastened to reproduce it in an enclosure void of air, in order to avoid the combustion of the carbons. He saw that it could be enlarged, that the carbonaceous material was carried from the positive to the negative pole, that the former was more luminous than the latter, but that the general aspect of the phenomenon did not change. Despretz repeated the experiment with a more energetic battery, and ascertained that the carbon volatilized under the electric action was deposited on the sides of the glass balloon as soon as the intensity of the current exceeded a certain limit. It is probable that this deposition of carbon takes place in all cases, but does not begin to be ascertainable until the intensity is very great.

Things happen quite otherwise when instead of a battery a Ruhmkorff induction-coil is employed. It is known that it gives rise to successive induction-currents in opposite directions: the first currents, inverse, have too little tension to clear the distance separating the points, and produce nothing; the second, direct, acquire at last an enormous tension, but have little duration and transport but a slight quantity of electricity. The whole therefore reduces to successive almost instantaneous discharges separated by comparatively prolonged intervals of rest, to sparks, and *in vacuo* to emanations of light; but there is never an electric arc, because the quantity of electricity is insufficient.

Gramme machines with alternating currents participate at the same time in the properties of batteries and the induction-coil, while presenting some special characters: they give two alternately contrary currents; but these are equal, last the same time, are separated by only a brief interval, and transport, on account of their duration, a large sum of electricity. They could be replaced by a battery the direction of which changed periodically and without interruption; but they differ from a battery by the great intensity of their currents: when one of these is ending it is augmented by the extra current; when commencing, it profits by the inverse electromotive force of the preceding current, as I have demonstrated\*. In short, the effects will be those of batteries with an aggravation due to the enormous tension, and those of the induction-coil with the aggravation resulting from a larger quantity of electricity. This is verified by experiment. In air, instead of a single arc, several can be lighted; and the number of them is multiplied by increasing the tension—that is, by diminishing the section and increasing the length of the induced wire as well as the velocity of the rotation. This has permitted me to maintain sixty

\* *Comptes Rendus*, t. xcii. p. 1201.

lights by a machine which originally supported only eight. The results in the imperfect vacuum of an air-pump might yet have been in part foreseen; and they are very curious, as you will see, and as I have just observed with the cooperation of one of my pupils, M. G. Maneuvrier.

Taking an electric egg, I placed in it, face to face, two carbons of 15 centim. length, 4 millim. diameter, separated by an interval of 4 millim. When the exhaustion reached about 12 millim. the light began to spirt out spontaneously, not in the form of a brilliant arc confined between the points, but starting from all parts of the carbons, with the ordinary appearance of the emanations in Geissler's tubes. Each of them showed, at the same time, the appearances which, with the induction-coil, characterize the two poles—that is to say, the blue aureole enveloping the surface of the two cylinders, which belongs to the negative pole, and, besides, the paler stratified light due to the positive pole. It shot forth normal to the outline of the carbons; and the whole balloon was filled with light. The experiment is one of the most beautiful to be seen.

Thus the two currents contribute each an equal share to the production of the phenomenon, which is that of the Geissler tubes, but which assumes an incomparable splendour because of the considerable quantity of electricity that passes and rapidly modifies the observed appearances. In fact the carbons become heated, redden, and arrive at a pale whiteness, not only at their extremity, but throughout their length; they are then rapidly volatilized by the combined effect of the heating and the currents. Whatever may be the cause of this volatilization, it is certain that a carbonaceous material is diffused in the state of vapour. The balloon becomes filled with a blue gas very similar to iodine vapour, which deepens more and more in colour to indigo. After this the vapours condense abundantly upon the sides of the balloon, which become opaque; and this terminates the experiment. The deposit collected resembles finely divided carbon, and dissolves with effervescence and incandescence in nitric acid. Is it pure carbon, or a hydrogenated compound of carbon? That is a question which I reserve for ulterior examination.

To avoid this forced termination of the experiment, I have replaced each carbon by two equal bundles of crayons fitted to the two rheophores, and diverging in the direction of the generatrices of two cones with their bases opposite. In this case the currents divide into a great number of emanations less intense than the single one; all the carbons become luminous at once; and the more numerous they are, the less heated do they become. There is almost no volatilization; and the effect is prolonged as much as one pleases.

I have replaced the carbons by copper rods of 3 millim. diameter and diverging from the rheophore. The same effect is produced with still greater splendour. If the current is too intense, the copper melts. It is always in part volatilized, and is deposited in a thin coat upon the balloon. It is evident that the experiment



will be varied by employing different metals, different gases, and working under different pressures; I shall have the honour of making known to the Academy the results.—*Comptes Rendus de l'Académie des Sciences*, May 8, 1882, t. xciv. pp. 1271–1273.

ON THE EMPLOYMENT OF ROTATING DISKS FOR THE STUDY OF COLOURED SENSATIONS. THE RELATIVE INTENSITY OF COLOURS. BY A. ROSENSTIEHL.

In continuing my researches upon the coloured sensations, I have been led to examine a problem which has hitherto appeared inaccessible—that of the relative intensity of colours. What common measure can there be between a red and a yellow, a blue and a violet? It seems at first sight impossible to set up a numerical comparison between values which appear so different in kind; and yet this comparison is possible, thanks to a well-known special property of the eye.

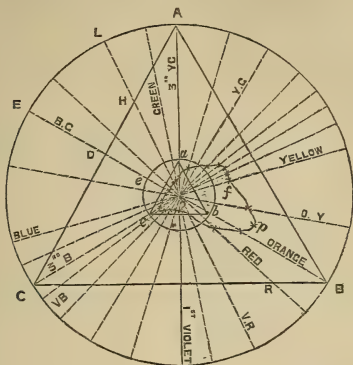
Between the different colours which have received names an infinity can be intercalated which form the insensible transition from the one to the other without a break. The series is continuous, and closes upon itself like the perimeter of a polygon. Besides (and I cannot sufficiently insist upon the peculiarity), this whole includes an infinity of sensations which, associated in twos, produce a sensation identical for all, *that of white*. We find nothing analogous in the sensations of the ear; and it is this highly characteristic circumstance that gives a common measure between the different colours.

In my previous Notes, adopting and precisely defining Young's theory, I laid it down as a principle that the sensation of white results from the *equal* excitation of three primary sensations. Consequently every pair of complementary colours represents in its combination the mixture of the three primary colours *at equal intensity*. This notion of equal intensity was introduced into a graphic construction, which was discussed; and I verified the principles on which it is based.

It is necessary to distinguish between intensity of coloration and total luminous intensity. By adding the sensation of white in different proportions to a coloured sensation of constant intensity, colours of the same intensity of coloration, but of different total luminous intensity, are obtained. These colours have for their common measure the angle of the sector of the complementary necessary to extinguish all coloured sensation; and, generally, *the angle of the sector of the complementary colour is in the inverse ratio of its coloration-intensity. The angle of the white sector\* is in the direct ratio of the total luminous intensity.*

\* It will be remembered that, in all my experiments, the intensity of the sensation of white is measured by the angle of a sector painted white with sulphate of barium, which is set in rapid rotation in front of an absolutely black orifice.

When the colours have not the same complementary, the graphic construction is indispensable for the determination of the intensity.



From the point O, I draw three lines  $OA=OB=OC$ , the length of which is proportional to the intensity of the colours A, B, C, which I regard as primary sensations, and which, for that reason, are placed at an angular distance of  $120^\circ$  from one another. The places of the colours resulting from the mixture, in twos, of the three primary sensations are necessarily upon the sides of the triangle ABC. Their distances from the vertices are in the inverse ratio of the coloured sectors necessary to produce them; and their distances from the point O represent their coloration-intensities. In this conception the point O is not regarded as the centre of gravity of the triangle; it represents not the place of the white, but the *absolute black*.

The intensity of the binary colours being given by the construction, it is easy, with the aid of rotating disks, to compare with it the coloured surfaces the intensity of which we wish to know.

Let there be required to find the intensity of coloration of a red surface S. I mix C and B so as to obtain red, which I reproduce, in another part, with a sector S, of which the angle  $\alpha$  is given by experiment. Let R (in the figure) be the point occupied by the red; we have

$$\frac{OR}{OB} = I \frac{\alpha}{360},$$

from which we get for the intensity of coloration I of the surface S

$$I = \frac{OR \times 360}{\alpha \times OB}.$$

This method is susceptible of verification. Knowing the in-

tensities of two complementary colours, we know the ratio of their intensities. From this ratio we deduce the angles of the sectors which ought to reproduce the sensation of white—a condition easily verified by direct experiment. The following Table contains the result of this measurement for ten pairs of complementary colours copied upon the chromolithographed circle by M. Digeon, from the chromatic circle of M. Chevreul, whose nomenclature I have retained.

	Ratio of the coloration-intensities, given	
	by the construction.	by direct experiment.
3rd yellow-green and violet .....	1·17	1·25
4th green and red .....	3·72	3·73
Blue-green and orange .....	6·80	6·70
1st blue-green and orange-yellow ..	6·28	6·20
Blue and yellow .....	3·74	3·80
2nd blue and 1st yellow.....	3·13	3·18
3rd blue and complementary yellow	3·07	3·00
4th blue and 2nd yellow.....	2·16	2·21
Violet-blue and 4th yellow.....	2·16	2·13
2nd violet-blue and yellow-green ..	2·18	2·00

The accordance between experiment and construction is one of the most complete, so that the latter can be regarded as summing up exactly the state of our knowledge respecting the mixing of colours. It gives for each the proportion of the primary sensations CR : RB, the coloration-intensity OR, the complementary V, the ratio of the sectors of a pair of complementary colours  $\frac{OR}{OV}$  ne-

cessary to produce the sensation of white, the intensity of that sensation, the total luminous intensity, the triads, &c.

Having obtained all these concordant numerical results, I could not resist the desire to advance a step further and examine if it was possible to express the intensity of a colour by its ratio to that of white, and thereby to learn what is the distance which still separates the finest colours obtained with colouring-matters from those which the eye is susceptible of perceiving.

In regard to the total luminous intensity that ratio has been exactly determined. The finest aniline-blue represents only one fifteenth, and the chromates of lead one seventh, of the intensity of the white obtained, for one and the same illumination, with barium sulphate. For the coloration-intensity the difference would be still greater; and hence it is evident that the chemistry of colouring-matters owes us yet much progress before it can realize what light can give us and what the eye is capable of perceiving.—*Comptes Rendus de l'Académie des Sciences*, May 22, 1882, t. xciv. pp. 1411–1414.

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Fig. 2.



Fig. 3.



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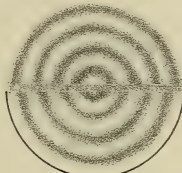


Fig. 5.



Fig. 6.



Fig. 7.



Fig. 8.



Fig. 9.



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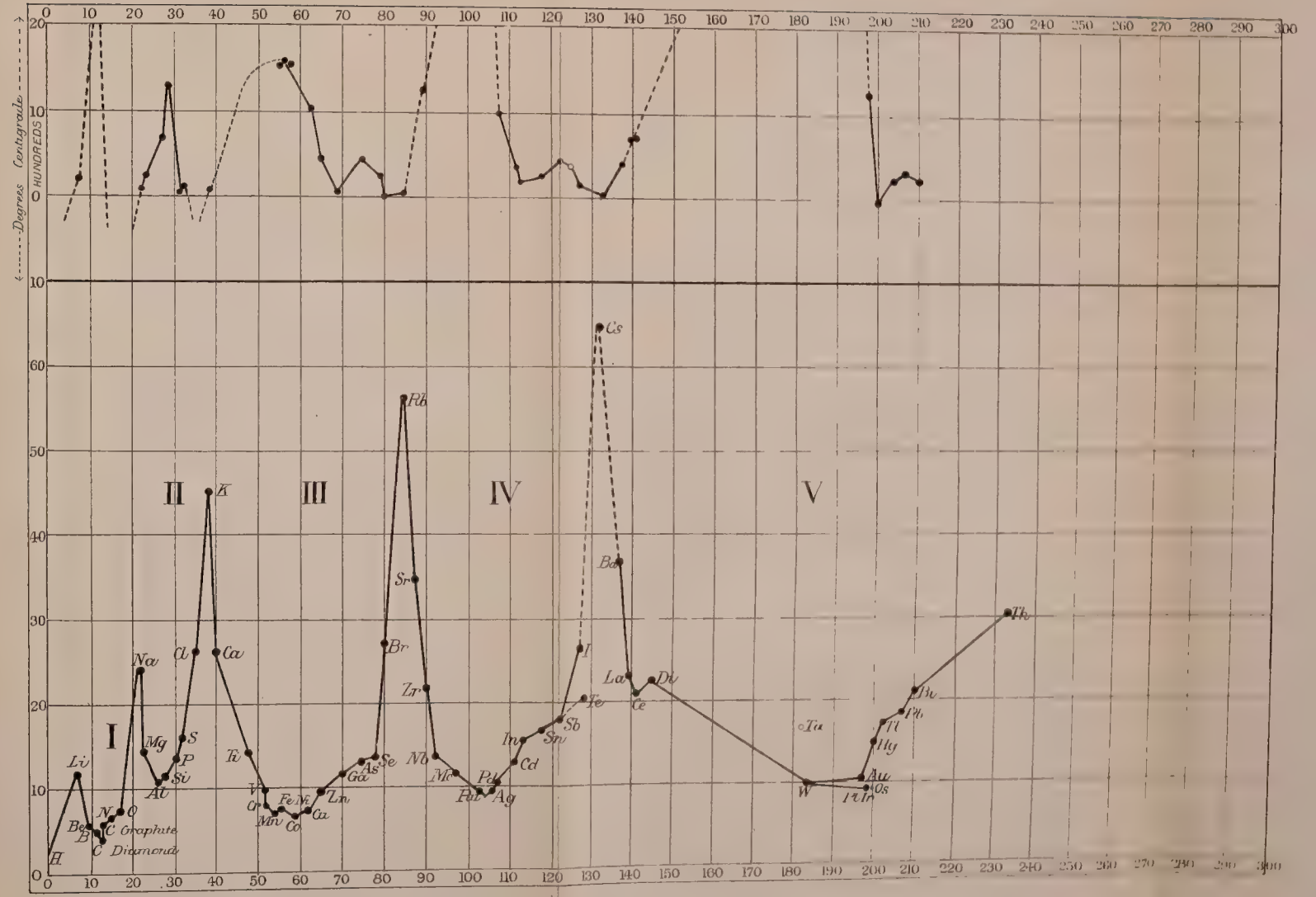
Fig. 11.



Fig. 12.



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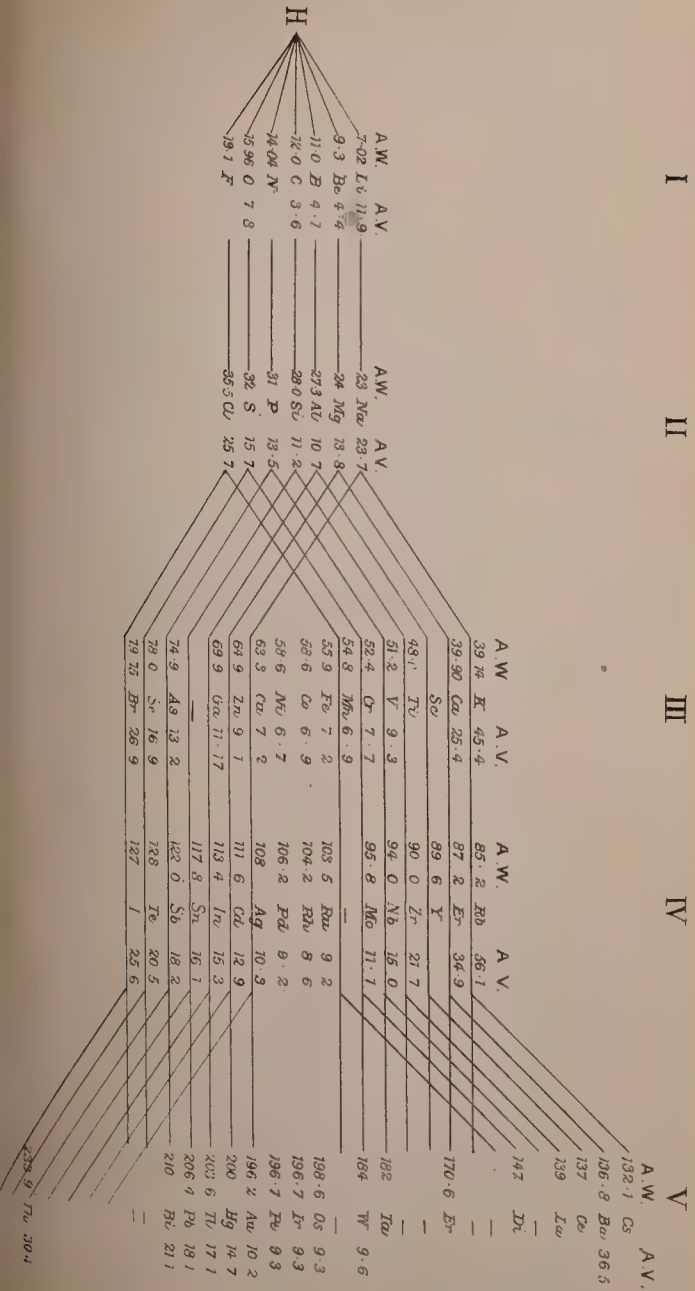
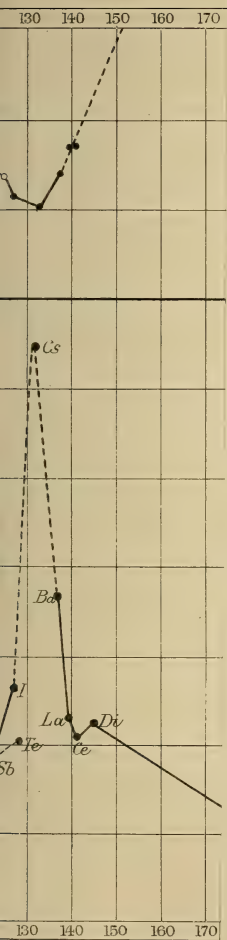


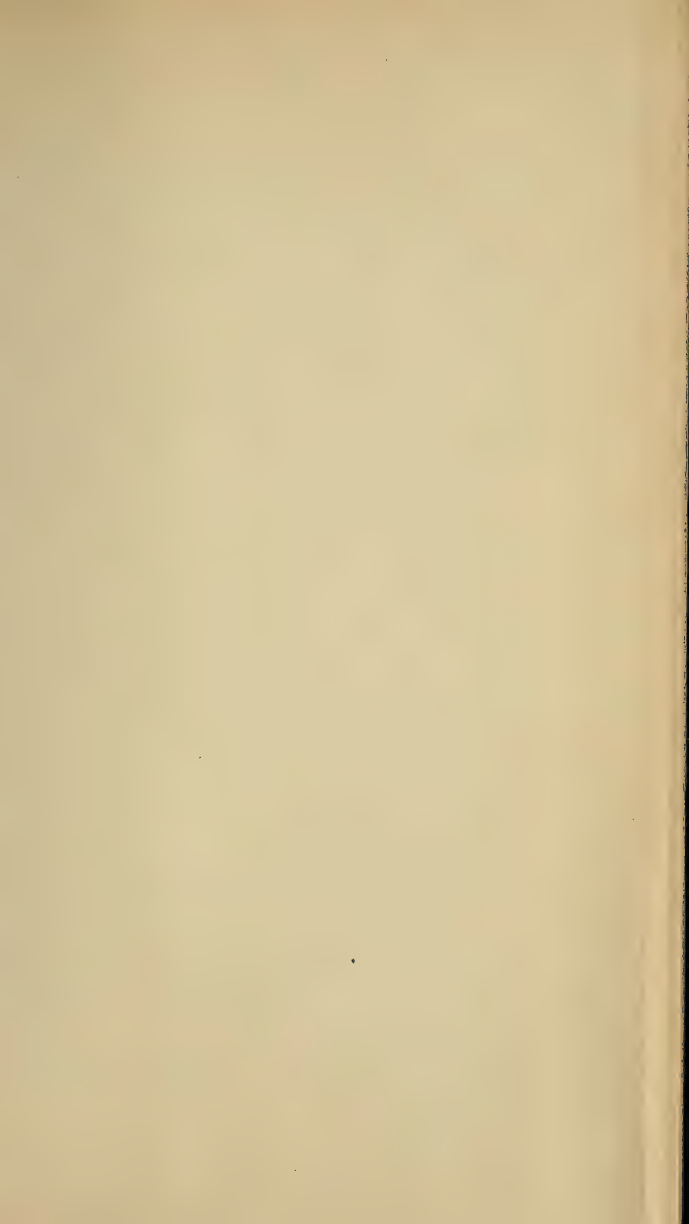




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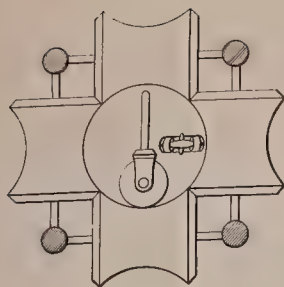


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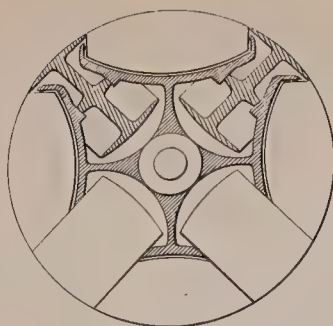


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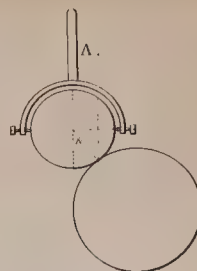


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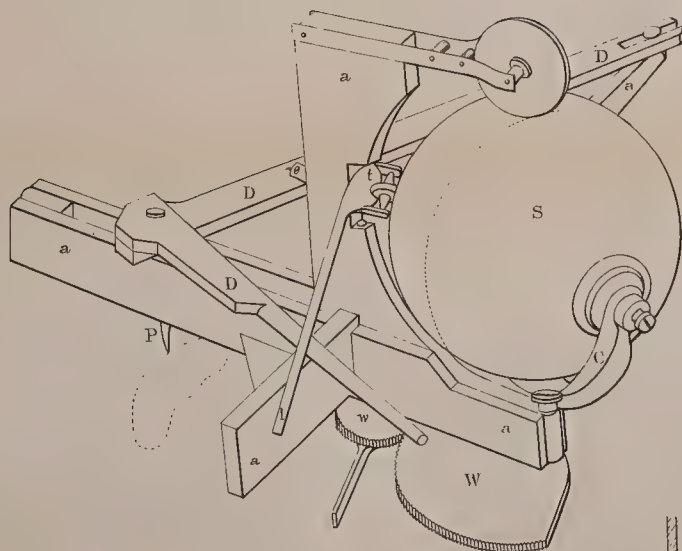


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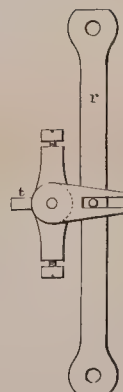


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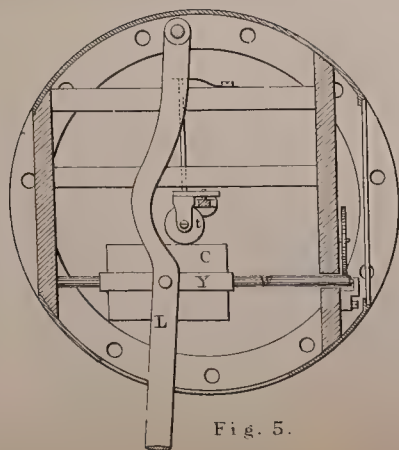


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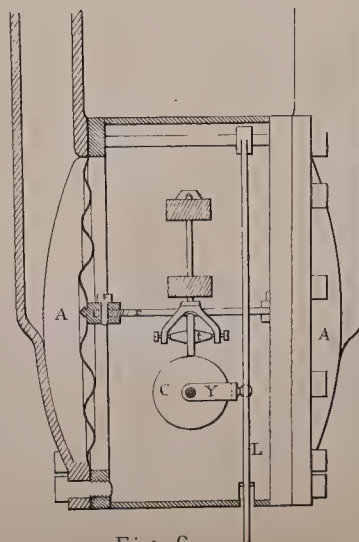


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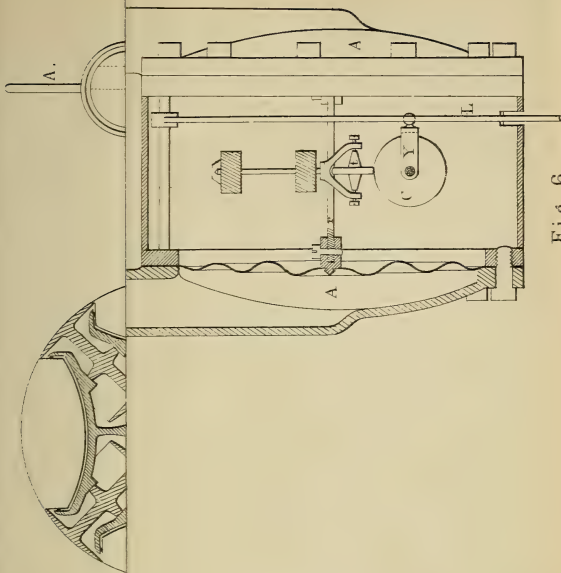


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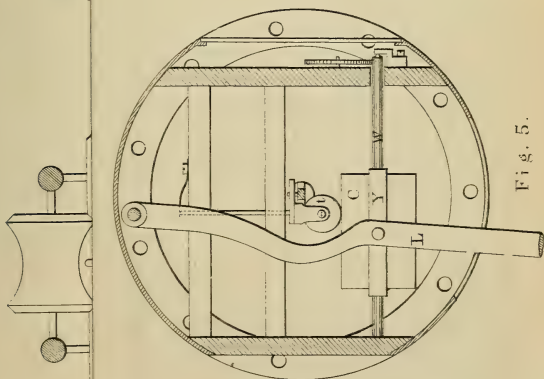


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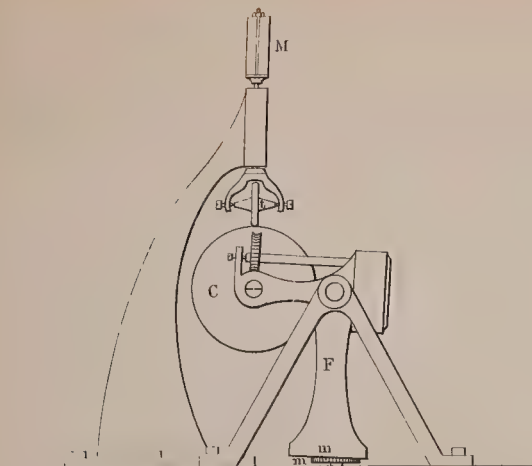


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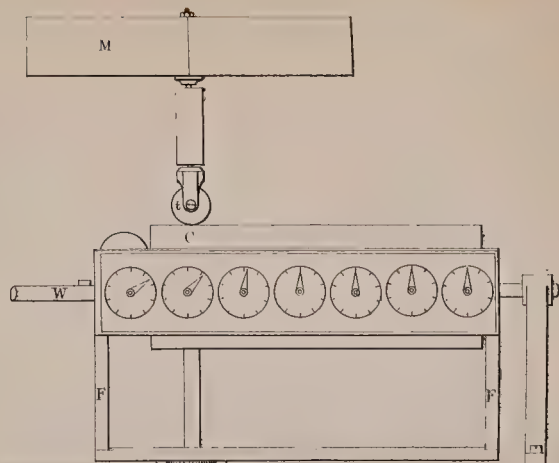


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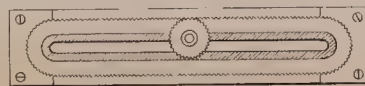


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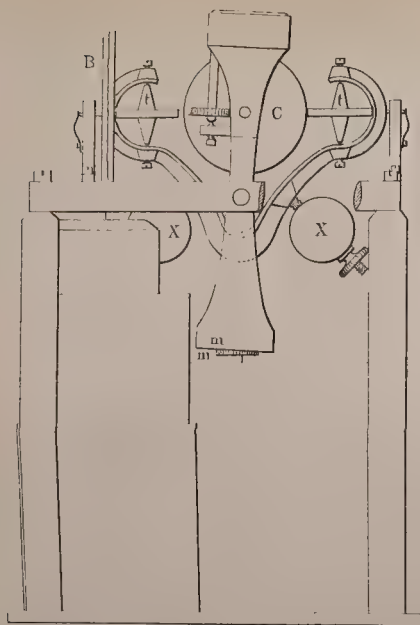


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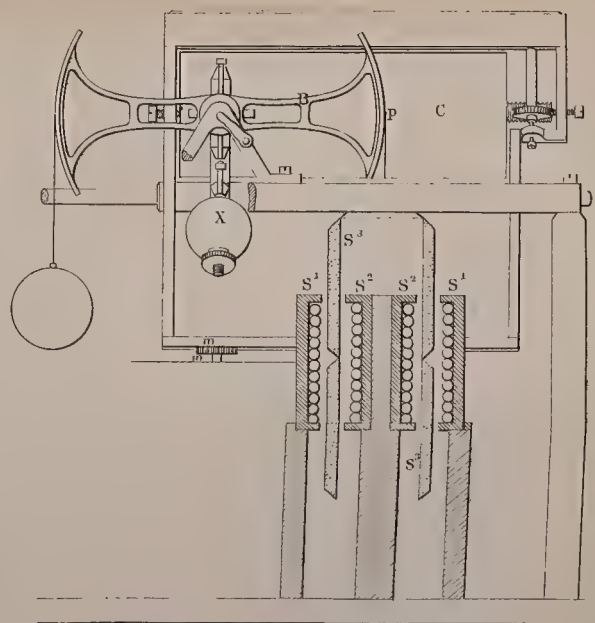


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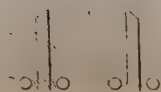


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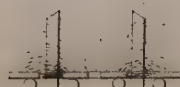


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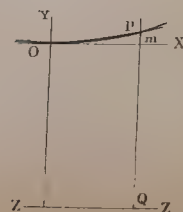


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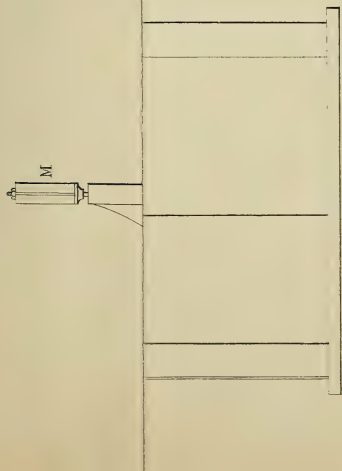


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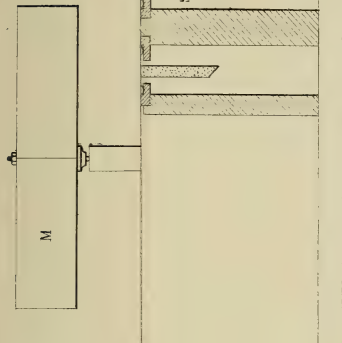


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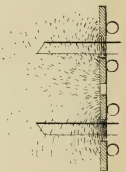


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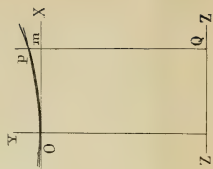


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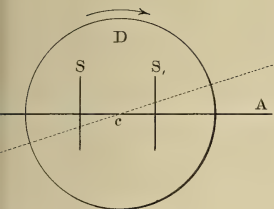


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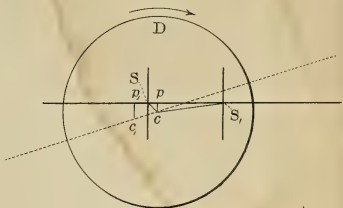


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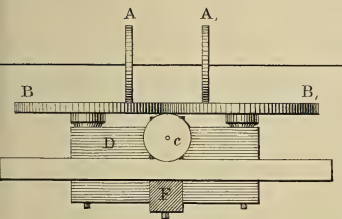


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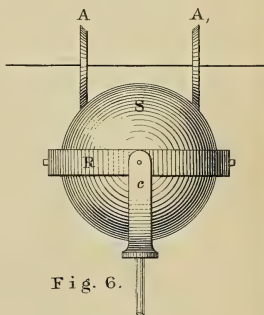


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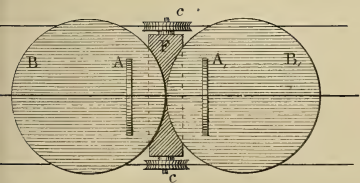


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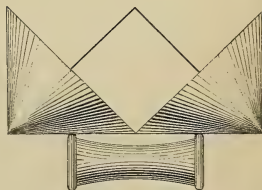


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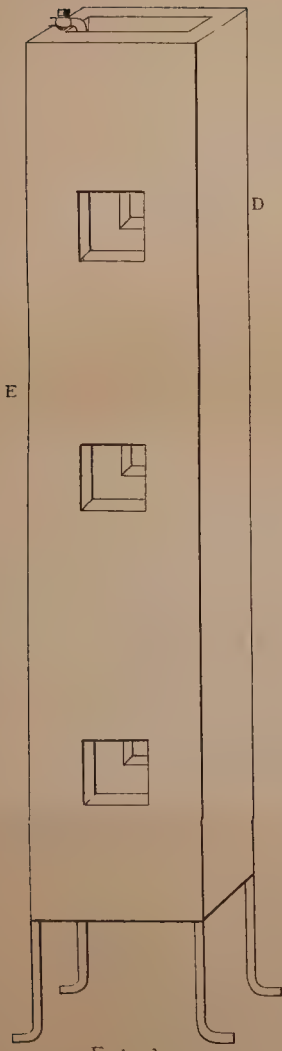


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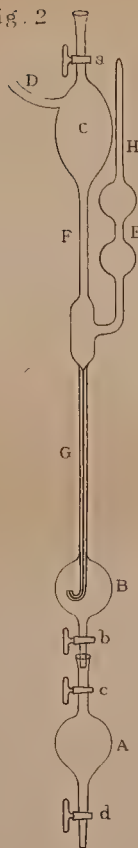


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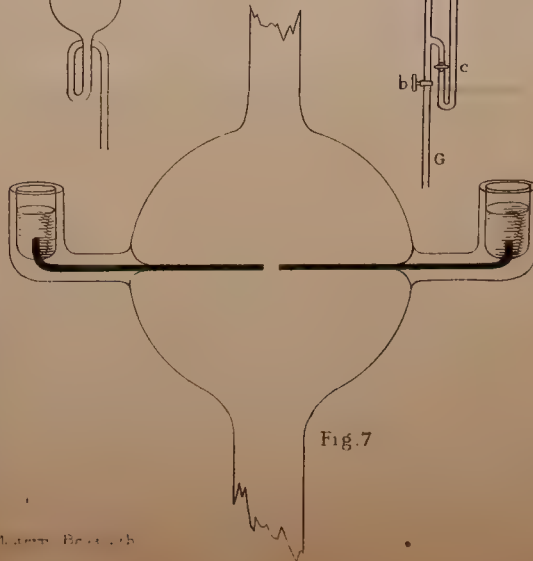


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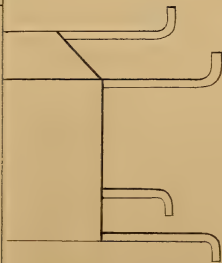


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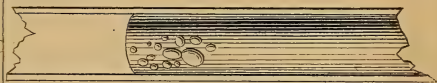


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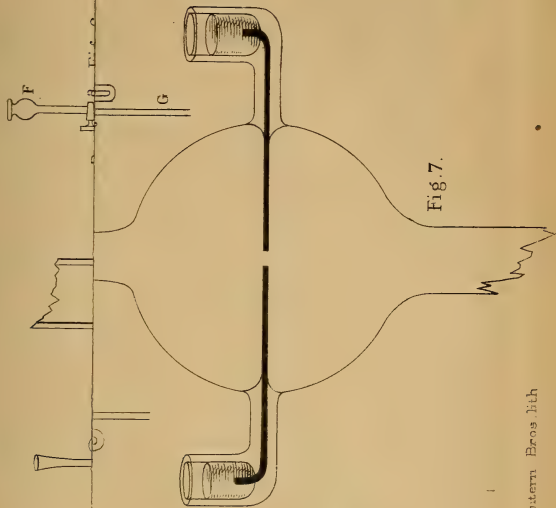
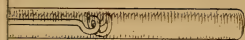


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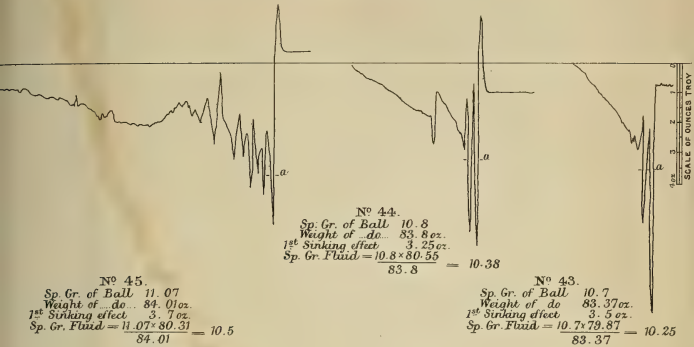


## DIAGRAM N° 1.

May 6<sup>th</sup> 1881.

Experiment on 3" Lead Balls melted in Fluid Lead.

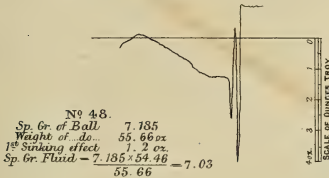
Note. — The lead was very hot during Exp<sup>t</sup> 43.  
and gradually cooled during Exp<sup>s</sup> 44 & 45.



## DIAGRAM N° 2.

May 18<sup>th</sup> 1881.

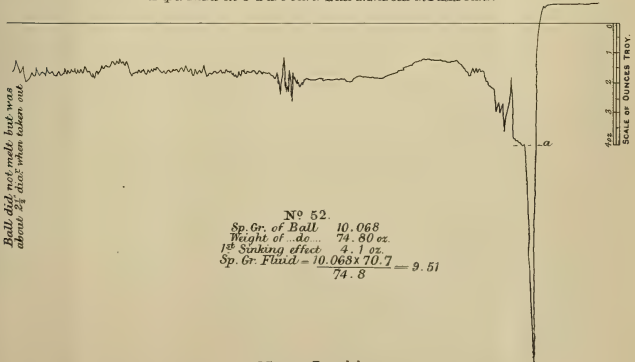
Experiment on 3" Tin Ball melted in Fluid Tin.



## DIAGRAM N° 3.

Aug. 18<sup>th</sup> 1881.

Experiment on 3" Pure Silver Ball immersed in Fluid Silver.







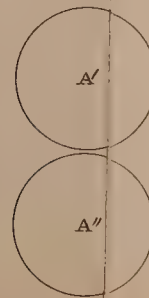
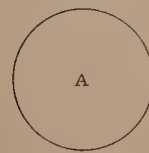
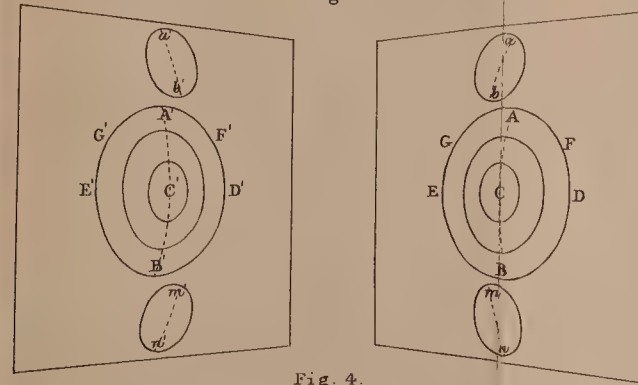
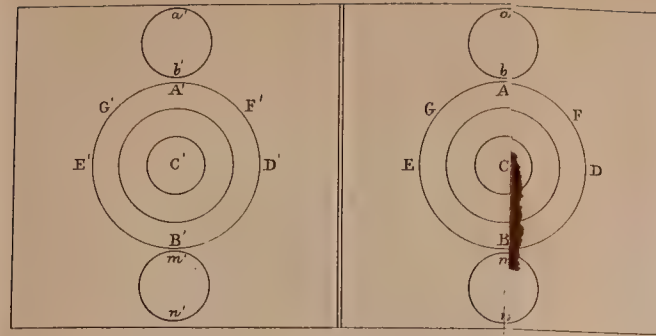
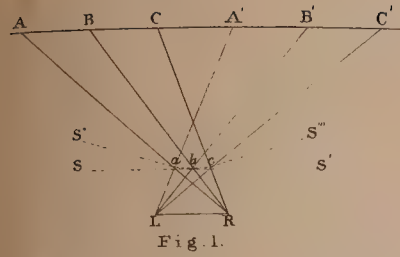
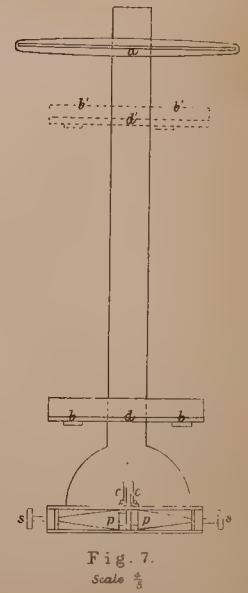
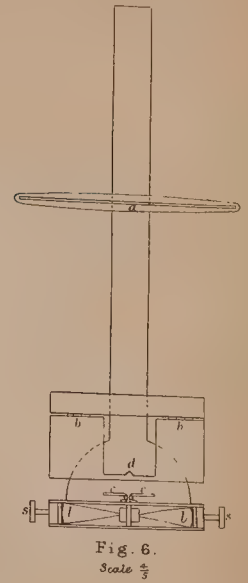


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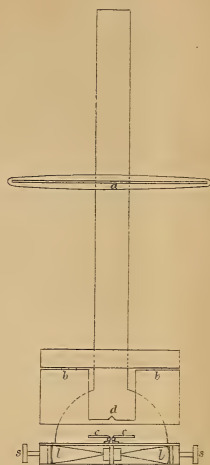
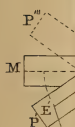
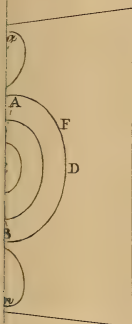
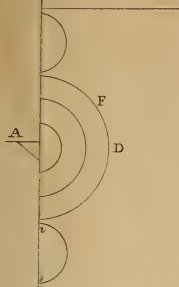


Fig. 6.  
Scale  $\frac{4}{5}$



Fig. 7.  
Scale  $\frac{4}{5}$





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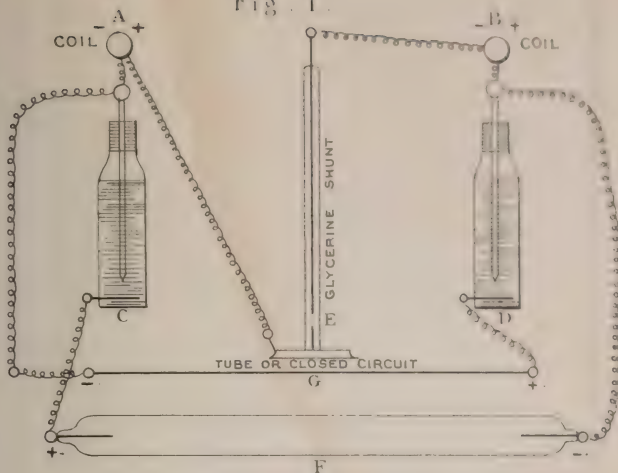
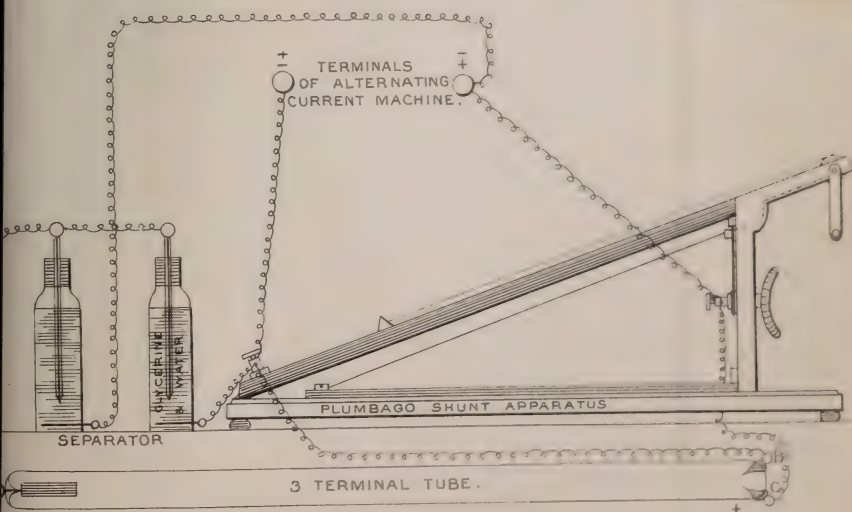


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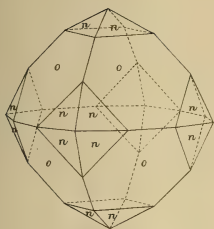


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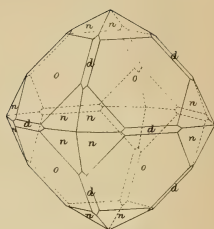


Fig: 2.

- $o$  (111)
- $d$  (110)
- $a$  (100)
- $n$  (211)
- $f$   $\pi(310)$
- $s$   $\pi(312)$

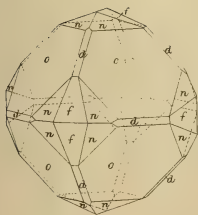


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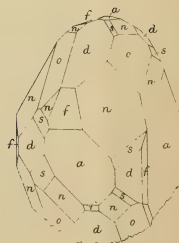
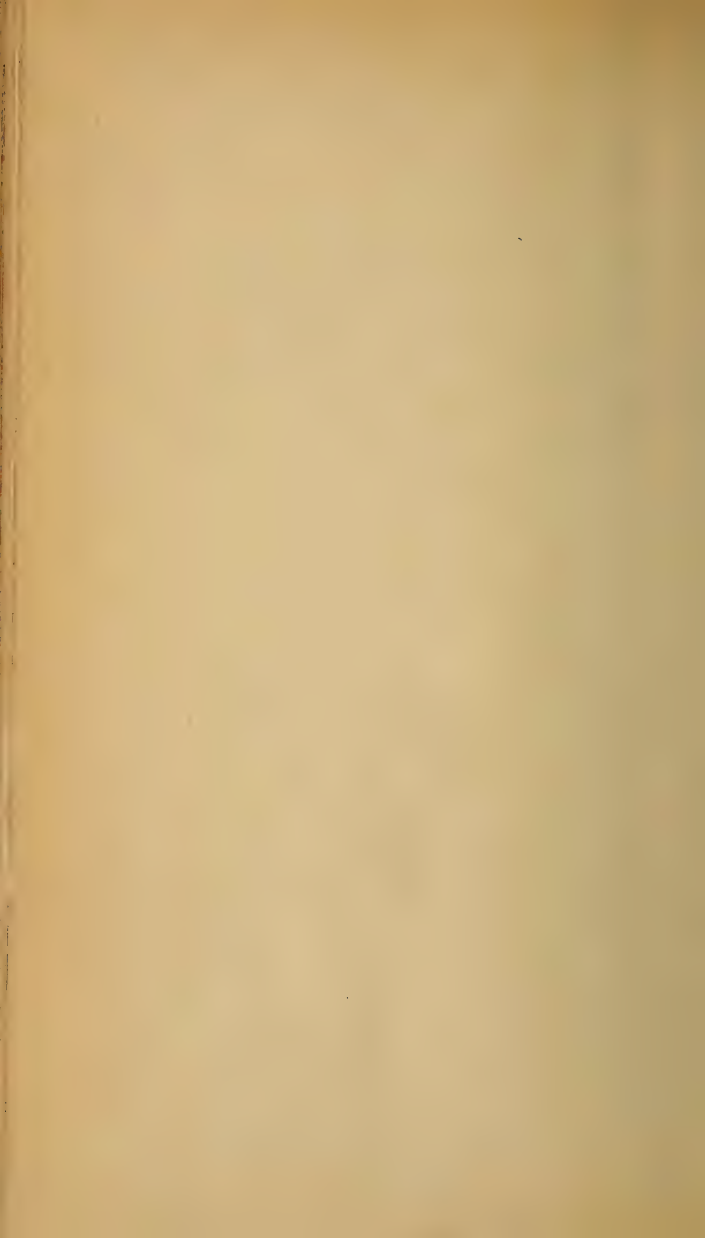


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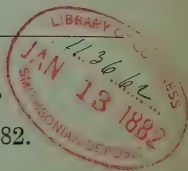
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burgh; Smith and Son, Glasgow;—Hodges, Foster and Co., Dublin;—Putnam,  
New York;—and Asher and Co., Berlin.

P. 414, for E. H. Nichols read E. L. Nichols.

*Errata in No 78 (January 1882.)*

Page 45, end of art. 45, for  $+e_2$  read  $-e_2$

— 46, art. 50, line 6, end of numerator, for  $\frac{3}{2^n}$  read  $\frac{3}{2^n} J$

— 46, art. 52, line 4, for (13) read  $f(D)_2 z + x^3 F(D)_2 z = 0$  . (14)

— 46, art. 52, line 5, for (13) read (14).

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*Errata in Vol. XII. (November 1881).*

Page 370, second line from bottom, *for maximum velocity read maximum rate of change of velocity*

— 371, second line from top, *for kinetic energy read acceleration*

*Errata in No 79 (February 1882).*

Page 135, last line of text, in equation (7), *for  $\frac{\Theta}{\Theta_c}$  read  $\frac{\Theta_c}{\Theta}$*

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